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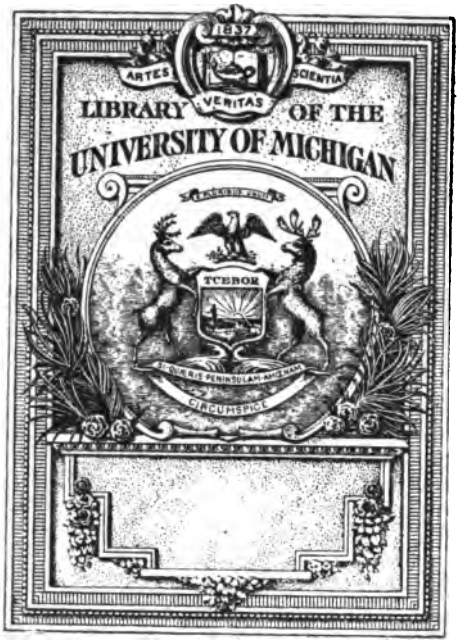

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THE CHEMICAL NATURE OF A COLLOIDAL CLAY

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DISSERTATION

PRESENTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN THE GRADUATE SCHOOL OF THE OHIO STATE UNIVERSITY

By
RICHARD BRADFIELD

The Ohio State University
1922

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THE CHEMICAL NATURE OF A COLLOIDAL CLAY

RICHARD BRADFIELD

Abstract.—The fresh subsoil of Putnam silt loam, predominating prairie soil of Northeast Missouri, was suspended in five parts of water by churning, the coarser material settled by gravity and the finest colloidal material separated by means of a centrifugal force of about 30,000 times gravity. This fraction was unusually high in Al^2O^3 and Fe^2O^3, almost all of which was soluble in hot HCl. This indicated that the colloidal fraction might be made up largely of the completely broken down end products of weathering; colloidal Al^2O^3, Fe^2O^3 and SiO^2. A synthetic mixture of these colloids having a chemical composition similar to the natural colloid was prepared and their physico-chemical properties compared. Cataphoresis studies showed that the natural colloid was negative and that the synthetic mixture was positive. The migration velocity of the natural colloid was decreased by traces of acids and increased by traces of alkali; larger amounts of alkali caused flocculation. In no case was the direction of migration reversed. The synthetic colloid had a much stronger buffer action than the natural colloid due apparently to its high content of free Al^2O^3. The natural colloid was flocculated most readily by polyvalent cations in an acid medium. The synthetic mixture was more sensitive to polyvalent anions and to alkalis. Analyses were made of the fractions of each colloid soluble in dilute acid, and in dilute alkali. The differences were marked throughout. All data obtained indicated that the natural colloid was a complex alumino-silicate, rather than a mixture of the separate colloidal oxides.

The Putnam silt loam, which is the predominating soil type on the level prairies of northeastern Missouri, is underlaid at a depth of 12 to 20 inches with a very heavy clay layer. This heavy layer is so compact that there is practically no water or air movement through it, except when it is cracked by drought. For this reason crops growing on it suffer severly in periods of wet weather, for the surface soil is kept saturated until the excess of water is removed by surface evaporation. Crop yields are probably reduced even more by the drought periods in the summer, because the supply of moisture stored in the surface and subsurface layers is soon exhausted, and there is little available from beneath.

The imperviousness of the heavy layer is due to the fact that a large proportion of the particles are so extremely small and consequently fit so closely together that there is not enough effective pore space to allow any appreciable passage of either air or water. Tile drains laid in the heavy layer function very poorly.

The object of this investigation was to isolate the colloidal

M.K.

material found in this subsoil and to study its principal physical and chemical properties with the hope that such studies might furnish some information that would be of value as a basis for field experiments of a more practical nature. This study includes the following: (1) A centrifugal method for separating the colloidal material from the soil. (2) The preparation of a synthetic mixture of colloidal $Al(OH)_3$, $Fe(OH)_3$ and H_4SiO_4, having the same total analysis as the natural colloid. (3) A comparative study of some of the physico-chemical properties of the natural colloid and the synthetic mixture. (4) An interpretation of the comparative physico-chemical studies showing the probable chemical combinations existing in the natural colloid.

METHODS OF SEPARATING COLLOIDAL MATERIAL FROM SOILS

Review of Literature.—The term "colloid" as applied to soils by different investigators has been used to cover a considerable range in size of particles. Hilgard[32]* regards as colloidal all material which will remain in suspension for 24 hours in a column 8 inches high. In the recent work done by the Bureau of Soils[24] 1 micron has been considered the upper limit for colloidal clay. In this study the term is applied to that portion of the soil whose particles are invisible under the high-power direct-vision microscope, which show no tendency to settle out, and which are less than 0.1 micron in diameter. Most of the studies are made only on that fraction of the colloidal material which was physically homogeneous.

Because of the effect of colloidal material on the physical properties of soils, considerable work has been done on the development of some fairly accurate means of estimating the quantity of colloidal material present. Mitscherlich[41] devised a method based upon the water vapor adsorption of the dry soil. Ashley[2] devised a method based upon the adsorption of certain dyes. Rholand[50] pointed out that the different dyes were specific in their action; that is, some were adsorbed more strongly by one colloid, others by another.

While the above methods give results which are good indications of the quantity of colloidal material present they leave much to be desired when one wishes to make a more thorough study involving the physico-chemical properties of the colloids themselves.

*Refers to Bibliography, page 58.

For this purpose the separation of the colloidal material from the rest of the soil is desirable. Several such methods have been proposed, separation being brought about by differences in (1) solubility, (2) electrical charge, and in (3) size and specific gravity of the particles.

Horvath[33] found that the colloidal SiO_2 in soils was dissolved by heating the soil with 1% $NaCO_3$ for 15 minutes. Fraps[23] proposed a method for determining the inorganic colloid content of a soil based upon its solubility in 4% NH_4OH. The soluble colloid content of the soils studies varied from 0.0% to 6%. It contained from 47 to 60% SiO_2, from 11 to 24% Fe_2O_3, and from 8 to 37% Al_2O_3. In the soils containing the larger amounts of soluble colloidal material, the percentage of Al_2O_3 was much higher. While such solubility methods may give an indication of the amount of colloidal material and of its chemical composition, they are without value for the isolation of colloidal material for physico-chemical studies, because the properties of the colloid are changed during the solution process and it would be difficult if not impossible to restore them to their original colloidal condition after they had once been brought into true solution.

For the separation of finely divided suspensions Ormondy[45] devised a machine utilizing the negative charge of the clay particles. A drum of a non-corroding metal, which served as an anode, was revolved inside strips of copper placed around the anode at a distance of ¾ inch. The clay particles are drawn to the anode, water is driven off, impurities settle to the bottom, and the clay in a relatively pure condition may be scraped from the anode. Such a device is not suited to the present work, because considerable material not truly colloidal would be deposited along with the colloids. In addition, part of the colloidal material would give up its negative charge when it came in contact with the anode and would consequently have properties different from the natural colloid.

There remains the possibility of utilizing the difference in size of particle and specific gravity for effecting a separation. Schloessing[25] allowed suspensions of clays to stand undisturbed for long periods. Several distinct strata developed. The upper stratum, which never settled, was found to be made up of particles invisible under the highest-powered microscope. When removed and dried, this material formed a translucent, horny mass. The lower layers he considered to be made up of mixtures increasing in complexity as the bottom of the vessel was approached. While this method

yields colloidal material with its natural properties undestroyed, it has two great disadvantages. First, it is extremely slow. Months would be required to isolate enough material for a few simple determinations. Second, it would not give quantitative results, for a large part of the colloidal material would be carried down by the slow settling suspensions. Resuspension and resettling would effect a fairly complete separation if it were carried far enough, but such a fractionation would take years in some of our highly colloidal soils.

Separations requiring considerable time when subjected to gravity alone may be hastened by the use of centrifugal force. A very satisfactory method of separating colloidal material from soils has been developed in this laboratory and is described in the experimental section of this paper.

Effect of air drying on soil colloids.—Most soil studies are made on samples which have been allowed to become air dry. In nature this drying is probably never as complete as it is in the laboratory. This applies especially to heavy subsoils whose moisture content is usually rather high. Van Bemmelen[6], in his classical researches on the hydration and rehydration of gels, found that after a gel had been allowed to dry, its original moisture content could not readily be restored. Patrick[46] has recently shown that the adsorptive capacity of silica gels for certain gases was markedly influenced by their water content. When the dehydration was carried out in a vacuum, the adsorption was found to be reversible. This result lends weight to the opinion that the irreversibility of the dehydration of colloids is due partially to the adsorption during drying, of a layer of air which is very difficult to displace.

The beneficial effects of thorough drying on colloidal soils have been noticed for a long time. In India some of the natives make a practice of thoroughly drying their soils in the sun.

Mitscherlich[41] and Tacke and Immendorf[59] found that certain soils were irreversibly changed on thorough drying.

Ehrenberg and Pick[41] found that soils allowed to become air dry adsorbed less water than moist soils. For this reason they suggested that the moist soil be used in determining the hygroscopic capacity. They consider the difference due either to the effect of drying on the colloidal material itself or to a layer of adsorbed air on the soil granules.

Beaumont[5] found that the adsorptive capacity of soil colloids

for water decreases after drying but that new colloids are formed by clays standing in excess of water.

Tempany[61] found that the colloidal material of the soils of the West Indies could be restored by moistening and kneading the air dry soils.

Ceramists, according to Reis[49], commonly bring back the plasticity of clays by soaking them in water for several months. Mechanical grinding facilitates this "aging".

Scores of investigators have found that air dry soils have a higher soluble salt content than fresh soils. Colloids have a great capacity to adsorb soluble salts and retain them against leaching. Any factor which would cause a decrease in the amount of the colloidal material in the soil would cause a corresponding increase in the soluble salt content. It seems probable that many of the increases in soluble salt content occurring on drying the soil are due to the irreversible dehydration of the colloids. The extensive literature on this subject is summarized in a recent paper by Gustafson[26].

The impervious clay layer of the soil under study, the Putnam silt loam, according to the Bureau of Soils Report[12] weathers readily when brought to the surface and soon becomes about as productive as the surface soil.

This literature indicates the advisability of using fresh soils for the extraction of the colloidal material. A few preliminary experiments furnished convincing evidence.

Experimental.— *The effect of air drying on the amount of colloidal matter readily obtained from soils.*—A mechanical analysis was made of two samples of the subsoil, one fresh from the field, from which the original moisture had not been removed, the other from which the moisture had been removed by allowing it to become air dry in the laboratory. No deflocculant was used as it was not desired to introduce any chemical which would influence the condition of the soil. With this alteration the determinations were made by the usual Bureau of Soils method. The samples were in the mechanical shaker 7 hours.

MECHANICAL ANALYSIS

	Air dry sample	Fresh sample
Sand	27.0%	8.2%
Silt	50.2	34.65
Clay	23.8	57.1
	101.0%	99.95%

The difference in clay content is quite striking. Only 23.8/57.1 or 41.6% of the clay in the air dry sample was deflocculated by 7 hours shaking. The analysis of the fresh sample checks with previous analyses made on the air dry soil using plenty of ammonia as a deflocculating agent.

Since large quantities of the soil suspension were to be required, a churn of the barrel type operated at 50 r. p. m. was used to get the material into suspension. In the preliminary determinations, a proportion of one part of fresh soil (water content 26.5%) to ten parts distilled water was used. In order to test out more thoroughly the effect of air drying on the content of colloidal material readily separable from the soil, a sample of the air dry soil was weighed, enough water added to bring its water content up to that of the fresh soil, then an additional 10 parts of water were added for every part of the soil at the high water-content. This mixture was churned for 10 hours, duplicate 100-c.c. samples were removed at the end of each hour's churning by means of a pipette and allowed to stand in the ordinary 8-oz. shaker bottles for ten days. The fraction still in suspension was carefully poured off and the amount of oven dry material determined. A similar determination was made on the fresh soil. The data for this comparative test is given in Fig. 1. With the fresh soil, the curve flattens at three hours of churning. At that point 21.08% of the oven dry material was in suspension. Additional churning up to ten hours did not alter this percentage appreciably. With the air dry soil the percentage in suspension after three hours churning was only 5.14%, or less than one-fourth the amount obtained with the fresh soil. With additional churning, the colloid content increased gradually. At the end of ten hours the curve still slopes upward, but the colloid content is only 6.88%, or less than one-third that obtained with fresh soil under the same conditions.

The moisture equivalents of fresh and air dry samples were determined by the method of Briggs and Shantz. With the air dry soil the water content was 27.7% after centrifuging 40 minutes at 1,000 times gravity as compared with 32.5% for the fresh soil. These three experiments furnish conclusive evidence that the colloid content of the Putnam subsoil is altered sufficiently by mere air drying to make it advisable to use the fresh soil as a source of the colloidal fraction, if the conditions existing in the fields are to be approximated. They indicate also that it would be well to consider the effect of air drying of the samples in all studies of heavy

soils, for the effect on the colloid content will probably alter appreciably all other physical properties.

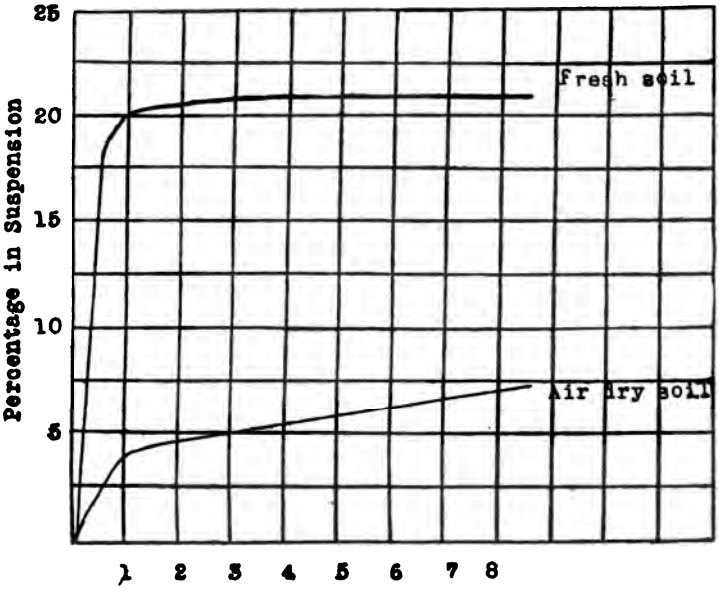

Fig. 1.—Effect of Churning on the Colloid Content of a Fresh and of an Air Dry Soil.

Methods of sampling and of storing samples.—Samples of surface, subsurface, and subsoil were obtained by careful spading and were placed in ordinary tinned, 50-pound lard cans, with tightly fitting lids, the cans being coated inside with paraffin to prevent rusting. After the samples were brought to the laboratory, the seam at the lid was also paraffined. This method of storage proved very satisfactory. The moisture content remained at about 26.5% for several months, and no difference has been detected between subsoils stored in this way for over a year and samples fresh from the field.

Effect of the soil-water ratio on the rate of sedimentation.—A determination of the relative amounts of material remaining in suspension when different proportions of soil to water were used, was made in order to find out the most logical proportion to use for later studies. The weights of fresh soil, given in the first column of Table 1, were placed in the ordinary 8-oz., wide-mouth shaker

bottles and 100 c.c. of distilled water added. This gave the soil-water ratios in the second column. The bottles were shaken in the mechanical shaker for six hours, then allowed to settle for 86 hours. The third and fourth columns give the weight of oven dry material still in suspension in duplicate samples. The amounts figured on a percentage basis are given in the remaining columns.

TABLE 1.—EFFECT OF RATIO SOIL/WATER ON PERCENTAGE OF MATERIAL IN SUSPENSION.

Weight of fresh soil	Weight of soil / Weight of H_2O	Dry weight of suspension		Per cent of material in suspension (fresh basis)		Av. percentage.
		1	2			
20.00	1:5	5.22	5.05	26.1%	25.2%	25.6%
10.00	1:10	2.41	2.07	24.0	20.8	22.4
6.66	1:15	1.20	1.12	18.0	16.8	17.4
5.00	1:20	0.981	0.90	19.6	18.0	18.8
4.00	1:25	0.595	0.628	14.9	15.5	15.3
3.33	1:30	0.529	0.499	15.8	15.0	15.4
2.50	1:40	0.337	0.350	13.5	14.0	13.7
2.00	1:50	0.215	0.258	10.7	12.9	11.8

As would be expected the per cent increases with the narrowing of the ratio. This is probably due largely to the fact that the viscosity is increased considerably in the more narrow ratios and consequently the solution offers more resistance to the settling particles. The results are presented graphically in Fig. 2. Because of the fact that there is no great change in the percent obtained with the 1:10 ratio and the 1:5 ratio and that the volume of suspension to be handled in order to obtain a given amount of colloidal material is only half as large with the latter, it was selected as the most logical ratio.

Rate of settling.—Previous experiments indicated that about 25% of the fresh subsoil remained in suspension for ten days. It was desired to find out the rate of settling in order to obtain an idea as to the relative amounts of the particles of different sizes. Three kilograms of the fresh subsoil were suspended by churning three hours with 15 liters of distilled water. The material was all kept in suspension during sampling by thorough stirring with the left hand while duplicate 200-c.c. samples were removed by

means of a pipette held in the right hand and placed in 8-oz. shaker bottles which were stoppered as soon as filled. The suspended

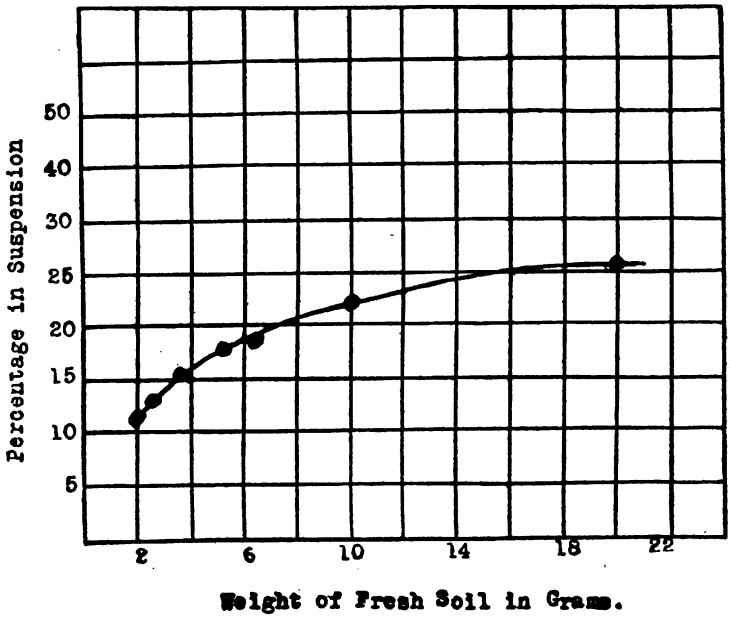

Fig. 2.—The Effect of the Soil-Water Ratio on the Rate of Settling.

matter was poured off of two bottles at frequent intervals during the first day when sedimentation was most rapid, and less frequently as the rate decreased. The data is calculated on the oven dry basis. A correction was made for the volume of the fresh soil calculated from the specific gravity (1.8). Two hundred c.c. of the suspension contained 26.46% of oven dry material when it was removed from the churn. The 26.46% therefore represents 100%. The results are presented in Table 2.

The data is presented graphically in Fig. 3. The most rapid settling takes place during the first 12 hours. All of the sand and silt and 23% of the clay comes down in this period. More than one-third of the clay or 20.9% is fine enough to remain in suspension for 26 days, and 16.5% or almost one-fourth of it was still in suspension after 50 days. The rate decreased very slowly after ten days, so it was selected as the most convenient sedimentation period.

After settling for 50 days the truly colloidal material, clear but

TABLE 2.—RATE OF SETTLING.

Settling period.	Wt. of material in suspension.		Average.	% of total (26.45 g..)
	1	2		
1 hour	13.23	13.20	13.21	49.7
1.75 hour	12.10	12.00	12.05	46.0
2.50 hours	11.39	11.38	11.38	42.8
12 hours	9.17	9.05	9.11	34.2
18 hours	8.41	8.99	8.98	32.9
24 hours	spilled	8.98	8.98	33.9
2 days	8.01	7.93	7.07	30.5
3 days	7.72	7.62	7.67	29.0
5 days	7.42	7.39	7.41	27.9
7 days	7.07	6.79	6.93	26.1
10 days	6.96	6.64	6.85	25.8
17 days	6.78	6.73	6.75	25.5
26 days	5.68	5.38	5.53	20.9
50 days	4.37	—	4.37	16.5

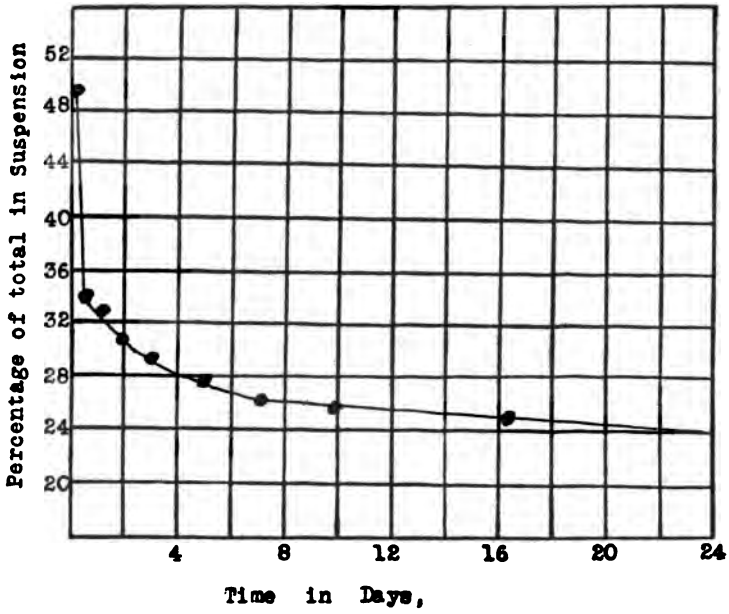

Fig. 3.—Rate of Settling.

with a reddish brown tinge, was noticed in only the top one-half centimeter of the vessel. The rest of the suspension was densely turbid. These facts show clearly that gravity alone would not make a satisfactory separation even though time were not a factor.

Separation by means of the super-centrifuge.—Preliminary trials with a milk clarifier, generating a centrifugal force of 10,000 times gravity, indicated that a higher centrifugal force such as is obtained with the Sharples Laboratory Supercentrifuge might be sufficient to throw out of suspension the great bulk of the colloidal material.

This centrifuge operated at 32,500 r. p. m generated a centrifugal force over 30,000 times gravity and threw out of suspension when fed at the rate of 1½ liters per hour all but 0.09% of the solid material. The larger particles, collected in the lower part of the bowl were a pale yellowish brown color and very stiff in consistency. In the upper portion of the bowl the deposit was thin, of a dark amber color but translucent when examined in thin layers. It was very greasy to the touch and barely viscous enough to cling to the bowl. The rest of the material was intermediate between these two extremes, there being a gradual transition from one to the other.

In the earlier work with the centrifuge the material deposited in the bowl was removed by scraping with a long spatula. On account of the small diameter of the bowl (2 inches) this method was found unsatisfactory when one wished to remove the total contents very carefully and in the exact order in which they were deposited. This difficulty was overcome by means of a device made as follows: The inside diameter of the bowl was carefully measured, its circumference calculated, and a rectangular piece of celluloid prepared which was of the same length as the inside depth of the bowl and the same width as its circumference. This was rolled up and slipped into the bowl. Its natural resilience held it firmly against the walls, forming a uniform lining or sleeve. After making a run, the bowl bottom was removed, a long, narrow, (¼ inch) sharp pointed spatula was slipped between the sleeve and the bowl and worked around the entire circumference. This loosened the sleeve so that it could be removed by seizing the two edges at the seam with a small pair of pliers and exerting a steady pull. By unrolling the sleeve the entire contents of the bowl were readily accessible. Division of the deposit could then be made at

any point desired and the entire deposit fractionated in almost a quantitative way by means of a spatula.

After numerous preliminary trials, the following procedure was found most satisfactory for the fractionation of the colloidal material: To facilitate centrifuging, it was desired to separate as much material as convenient by settling. A glance at the graph of settling (Fig. 3) shows that there is a flattening of the curve at the end of 10 days. This seemed the most convenient and logical settling period. Accordingly 1 part fresh soil (H_2O content 26.5%) was churned for 3 hours with 5 parts distilled H_2O, (Tap water brought about almost complete precipitation) allowed to settle for 10 days, then the suspension was siphoned off carefully, to avoid disturbing the material which had settled out.

This suspension was passed through the centrifuge at the rate of 10 liters per hour. This application proved sufficient to remove the bulk of the material. The material contained in the bottom 5 centimeters of the bowl was fairly homogeneous throughtout; it was saved and the balance discarded. The liquid coming through the centrifuge was a clear reddish brown when examined in thin layers through transmitted light, but a turbid, dirty brown by reflected light. It showed but very little tendency to settle on prolonged standing. This was passed through the centrifuge again at the rate of 1½ liters per hour. This application proved sufficient to remove all but about 0.09% of the colloidal material. The deposit in the bottom of the bowl after the second run resembled that in the top at the first centrifuging. It was discarded. The top half was covered with the viscous amber colored deposit apparently homogeneous throughout, and too fluid to adhere to the spatula when being scraped from the sleeve. The remaining fourth of the deposit was dark reddish brown in color, translucent in thin layers, but it was stiff enough to cling firmly to the sleeve. Because of this difference, it was separated from the material deposited in the top of the bowl. Later work shows that the material saved from the first centrifuging behaves as a typical suspensoid and that the two fractions saved from the second run have more of the properties of emulsoids. For convenience the first material deposited in the first run will be referred to hereafter as the Suspensoid; the fractions deposited last in the second run, including all fluid material, as Emulsoid A; while that fraction which is homogeneous, reddish brown in color, but too viscous to flow will be called Emulsoid B. When suspended in water sols A and B seem to be almost identical, B being only slightly lighter

in color. Later data indicate that the difference between them is largely in size of particles and degree of hydration.

Comparison with the Bureau of Soils method.—After this method had been developed, there appeared a description of a somewhat similar one developed by Fry, Middleton, and Moore of the Bureau of Soils[24]. These investigators use the same method of suspending their soils that is used in this study, but in other details the methods are quite different. These differences may be seen in the following table:

	Missouri Method	Bureau of Soils Method
Condition of soil	Fresh	Air dried
Suspending soil	Churn	Churn
Soil=H_2O ratio	1:5	1:5
Settling period	10 days	24 hours
Separation of Coarser particles	30,000 times gravity for 3 min. 3 x 30,000=90,000	17,500 gravity for 5 minutes. 17,500 x 5=87,500
Separation of emulsoid material (ultra clay)	30,000 x G. 15 min.	Pasteur-Chamberlain filters

The chief differences are that in this investigation the fresh soil is used, for the reasons presented above, while the Bureau workers use the air dry soil. They use a settling period of 24 hours, while in this study 10 days is allowed in order to facilitate centrifuging. The methods used for the separation of the coarser fraction are practically alike. The major difference is in the separation of the emulsoid material or ultra clay as it is termed by the Bureau of Soils workers. They use a Pasteur-Chamberlain filter and have the advantage of a somewhat more complete removal; for the Pasteur-Chamberlain filter will give a perfectly clear filtrate with the soil we are studying, while the liquid emerging from the centrifuge after the second run has about 0.09% of colloidal material still in it. This can be removed if the time of centrifuging is increased sufficiently, but inasmuch as it seems to be identical with that thrown down, except that it is slightly more highly dispersed, separation has not been considered advisable.

Three fractions with distinctly different physical properties can be separated from the liquid coming from the centrifuge the first time by means of the higher centrifugal force. All of this is deposited together on the walls of the filter tube when that method is used. In other words the term ultra clay as used by the Bureau investigators would include the material deposited in the bottom of the bowl in the second run, which was discarded in this work, as well as all of Emulsoid A and B. The differences between these fractions seem sufficiently great to make the separation advisable.

PHYSICAL AND CHEMICAL PROPERTIES OF THE SEPARATES OBTAINED

Physical Properties.— *Relative amount of each separate in the subsoil.*—A solution which had been allowed to settle for 30 days was found to contain 25% of the total amount of soil still in suspension. This suspension was passed through the centrifuge at the slow rate (1.5 liters per hr.). After the run the sleeve was taken out and the different fractions removed separately. The divisions adopted are of course arbitrary, and as the diameter of the bowl is reduced by the deposition of sediment there is an overlapping of the fractions of different size particles which is impossible to avoid. This overlapping may be minimized in quantitative studies by decreasing the amount of the suspension passed through in one run. The following percentages are presented as only rough approximations:

RELATIVE AMOUNTS OF THE CENTRIFUGAL SEPARATES

Amount separated by gravity in 30 days	75.0%
Emulsoid A	0.8
Emulsoid B	4.7
Suspensoid and intermediate	20.0
	100.0

The figures for the emulsoid fractions are doubtless low. In a subsequent experiment an attempt was made to wash all emulsoid material from the suspensoid. There was still an appreciable amount left after three careful washings. The fraction which settled out by gravity alone carried down with it considerable quantities of the finer separates.

Water Content.—The water contents of the emulsoid separates just as they were removed from the centrifuge were determined on the oven dry basis (105°).

Emulsoid A (finest)	82.35%
Emulsoid B	60.0 %

Linear shrinkage.—The linear shrinkage of the emulsoid was found to be 22.3% as compared with 12.7% for the suspensoid. It is of interest to note in this connection the limiting value assigned to the shrinkage of colloidal clay by Tempany[61]. He made a comparative study of internal pore space after full contraction with linear shrinkage and found a linear relationship. By extrapolating the curve thus obtained, an approximate limiting value for the shrinkage of "pure colloidal clay" was obtained. It was about 23%, a value in fair agreement with the experimental value obtained in this laboratory.

Size of particles.—The particles in the suspensoid are visible under the oil immersion microscope. They exhibit a marked Brownian movement and range from 0.4 to 1.2 microns in diameter. Zigmondy places the upper limit for colloidal particles at the limit of miscroscopic visibility, about 0.1 micron. According to his definition, the suspensoid would not be a true colloid. The particles of both emulsoids are invisible under the ordinary microscope but appear as light amber colored drops under the cardiod ultramicroscope.

Viscosity.—Solutions of both the emulsoid and the suspensoid containing 1 g. of oven dry material per 100 c.c. were prepared and their relative viscosity determined by means of an Ostwald viscosity pipette. The following table gives the average of six determinations of the time of outflow, all agreeing within 0.2 of a second. Temperature was 25°:

Distilled water	92.3 sec.
1% Suspensoid	94.4 sec.
1% Emulsoid	111.4 sec.

The suspensoid caused but a very slight change in viscosity at this concentration, while the time of outflow for the 1% emulsoid is 20% higher than water. These are the results one would expect with typical suspensoids and emulsoids.

Reaction and nature of charge.—The separates are both decidedly acid in reaction. The subsoil as a whole shows a lime requirement of over 6,000 pounds per acre by the Veitch method. The Sorensen value of a 0.1% sol as determined electrometrically and colorimetrically is about 5.0. No appreciable difference has been found in the reaction of the separates.

The particles of all separates when placed in an electrical field migrate to the anode and are precipitated there indicating a negative colloid.

Chemical Properties.—*Chemical composition.*—Analyses of the surface soil, subsoil, and of the suspensoid and emulsoid separates were made by the Official Methods. The amounts of each of the principal constituents soluble in concentrated HCl after two hours digestion on the water bath were also determined. The results of these analyses are given in Table 3.

TABLE 3.—RESULTS OF CHEMICAL ANALYSIS.

		Subsoil		Suspensoid		Emulsoid A	
Constituent	Surface	Total	HCl	Total	HCl	Total	HCl
SiO_2	75.09	60.88		47.81	0.14	45.49	0.16
Al_2O_3	9.63	17.94	11.41	23.13	20.00	24.54	24.28
Fe_2O_3	2.10	4.29	4.34	6.12	6.05	7.02	6.95
Ca O	0.39	0.36		1.75	0.42	1.66	0.64
Mg O	0.49	1.16		1.30	1.13	1.40	1.13
Na_2O	1.16	1.28		0.332		0.27	
K_2O	1.203	1.359		1.252		0.836	
MnO_2	0.27	0.22		not detr.	none	not detr.	none
TiO_2	not detr.	not detr	present	none	none	none	none
SO_3	0.144	0.122		not detr.	not detr.	not detr.	not detr.
P_2O_5	0.117	0.167		not detr.	not detr.	not detr.	not detr.
H_2O(105°)	2.98	5.56		8.29		9.88	
Volatile mater	4.20	6.11		9.94		10.27	
Insoluble					54.91		46.03
Totals	96.77	99.46		99.93		101.46	

These analyses bring out some interesting relationships: (1) The difference in composition of the suspensoid and emulsoid is not as wide as their physical properties would indicate. (2) All the Fe_2O_3 and Al_2O_3 in the emulsoid is soluble. (3) All iron in all samples is soluble in HCl.

The following table shows these relationships.

	Subsoil	Suspensoid	Emulsoid
Total Al_2O_3	17.94	23.13	24.54
HCl sol. Al_2O_3	11.41	20.00	24.28
% of total soluble	63.5	86.3	99.2
% of total insoluble	36.5	13.7	.8

Possible chemical nature of the emulsoid.—The analyses indicate that the emulsoid may be either:

(1) A complex silicate which can be completely decomposed by heating with concentrated HCl, the freshly precipitated SiO_2 being sufficiently dehydrated in the digestion to become comparatively insoluble in 5% Na_2CO_3.

(2) A mixture of colloidal SiO_2, Al_2O_3, and Fe_2O_3.

(3) A mixture of the simple oxides and the readily decomposable silicates.

The fact that it is not possible to extract all the Al_2O_3 from the suspensoid is evidence that we are dealing here with a mixture, a large part of which is soluble in HCl, but a very considerable portion of which is relatively insoluble.

The occurrence of soluble iron and aluminum in soils.—Many investigators have reported analyses of soils in which most of the iron and aluminum existed in forms which were soluble in ordinary acid and alkali solvents. Bauer[4] studied the soils of Madagascar and reports the following composition for a granite laterite. Concentrated hydrochloric acid was used as a solvent. For comparison the results of the hydrochloric acid analysis of the emulsoid from the Putnam clay are also given.

	Laterite	Emulsoid A
Insoluble	53.8	46.03
SiO_2	2.3	0.16
Al_2O_3	26.0	24.28
Fe_2O_3	3.8	6.95
CaO	0.3	(not detr.)
H_2O (over 100°)	13.8	20.25
	100.0%	99.44%

Lacroix[37] devoted a number of years to the study of the decomposition of the rocks of Madagascar. He concluded that the decomposition of granites, gneisses, micas, schists, etc., results

first in the formation of Al silicates, usually colloidal. They break down to form free colloidal SiO_2 and the colloidal hydrate of Al_2O_3. Iron always exists as the hydrate. In the zone of concretion the SiO_2 and other elements tend to be eliminated and Al_2O_3, more and more pure, tends to accumulate. There are in Madagascar almost complete transformations of the parent rock into colloidal aluminum silicates and aluminum hydrates.

Ulpiani[68] has studied the decomposition of rocks in southern Italy and has come to believe that the formation of laterite has been reducing the amount of clay in the soils of hot countries since the glacial epoch. Two types of soil have originated; one peculiar to the temperate zone, a superficial compact clay, the other peculiar to the torrid zone is a deep permeable laterite soil. The open character of the tropical laterite is probably due to the dehydration of the colloids which if thorough would result in the loss of colloidal properties.

Edwards[21] studied the analyses of a large number of the soils of the United States. Forty-four per cent of the analyses in which both free and combined SiO_2 were determined, showed an excess of Al_2O_3 over that required to form kaolin, which indicates the presence of free Al_2O_3. No free Al_2O_3 was found in glacial soils.

The similarity of the content of HCl soluble material found by Bauer in the tropical laterite and the finest centrifugal separate obtained from the Putnam subsoil is quite striking. Ulpiani shows that under temperate conditions lateritization may result in the formation of a very compact layer such as we have in Missouri.

Edwards' survey indicates that free Al_2O_3 may be present in a large proportion of the soils of the United States. In the light of these investigations it seems possible that we have in the emulsoid separate the end product of the weathering of the parent rock. Its presence may have heretofore escaped detection because it was masked by the great preponderance of the still undecomposed parent material. Lateritization has been considered of importance only in the tropics because only there has it gone to completion. The laterite of the tropics results in the formation of a permeable soil because of the dehydration of the hydrous colloids due to the extreme temperatures. The process has gone to completion there for the same reason. In temperate zones the decomposition would naturally proceed much slower in accordance with Van't Hoff's law.

DETAILED STATEMENT OF THE PROBLEM

A study of the principal physico-chemical properties of the emulsoid separate was desired as a basis for future work of a more practical nature. It was considered probable that if a synthetic mixture of colloidal silicic acid, aluminum hydroxide, and ferric hydroxide having the same composition as the natural colloid were prepared and its properties studied in connection with the natural colloid, such a study might furnish evidence on the form of chemical combination existing in the natural colloid; that is, whether we have in the natural colloid (1) the end products of complete decompostion, a mixture of colloidal SiO_2, Fe_2O_3, and Al_2O_3, (2) a highly weathered easily decomposed complex silicate, or (3) a mixture of (1) and (2).

With this object in view the synthetic mixture was prepared and a comparative study made of the properties of both the natural colloid, the synthetic colloid and of each of the constituent sols. These studies included (1) the velocity of migration, (2) the buffer action of the sols, (3) the minimum electrolyte concentration required for complete flocculation and (4) analyses of the fractions of the sols soluble in dilute acid and alkali.

PREPARATION OF A SYNTHETIC MIXTURE SIMILAR TO THE NATURAL COLLOID

Preparation of Constituents of the Synthetic Sol.—Sols of ferric hydroxide, aluminum hydroxide, and silicic acid were first prepared by the usual methods, and an attempt made to free them from the excess of electrolyte by dialysis. These methods were not well suited for the preparation of material for this study because of the following reasons: (1) they yield sols differing widely in size of particles; (2) it is very difficult to remove the electrolyte by dialysis; (3) the silicic acid is very unstable and is likely to form an "irreversible" gel on prolonged standing, even if it does not gel in the dialyser. This is especially likely to happen if the sol is rather concentrated. The natural colloid shows no tendency whatsoever to gel in the sense that Graham's silicic acid does. For this reason it was not considered advisable to prepare the silicic acid sol by this method. Kuhn[36] prepared a colloidal silicic acid that yielded a reversible precipitate (B silicic acid) by the hydrolysis of silicon sulfide, but this method could not be tried because silicon sulfide was not available. It is well known that certain precipitates, such as $Al(OH)_3$ and $Fe(OH)_3$, have a tend-

ency to become colloidal on prolonged washing. It seemed possible that if the washing were carried far enough, very stable sols might result. Ferric hydroxide and aluminum hydroxide were prepared from the chlorides of these metals by precipitation with ammonium hydroxide and silicic acid from sodium silicate by precipitation with hydrochloric acid. Large batches of each of these precipitates were placed in 12-liter bottles and washed with distilled water by decantation until they started to become colloidal. Additional washings were then made by means of the supercentrifuge. After four to six washings with the centrifuge the $Fe(OH)_3$ and $Al(OH)_3$ were sufficiently dispersed to yield very stable colloidal solutions with an electrolyte content much lower than that obtained by prolonged dialysis or by the hot dialysis method of Neidle and Barab[48]. The silicic acid precipitate required much more washing than the hydroxide of the metals but after prolonged washing a very stable opalescent sol was obtained. This sol showed no tendency whatsoever to gel. A detailed description of the centrifugal method of preparing colloidal solutions may be found in a separate paper[11]. The degree of dispersion of these sols was similar to that of the natural colloid, for they were deposited by the same centrifugal force.

Standardization of concentration of sols.—Fifty c.c. of each of the pure sols and of the natural emulsoid were placed in platinum dishes, evaporated to dryness, then placed in an oven at 105° for 24 hours and weighed. The residues were then ignited over a Mecker burner to constant weight. The loss on ignition which represents water retained at 105° was very large and varied widely with the different sols.

WATER CONTENT OF OVEN DRY RESIDUE FROM SOLS

Natural emulsoid	14.8%
Silicic acid	6.26
Ferric hydroxide	18.49
Aluminum hydroxide	35.82

These results show that if comparable quantities of the oxides are to be obtained, the concentration of the sols must be standardized on the water-free, ignited basis rather than on the oven dry basis.

Method of Mixing Sols.—Two of the constituent sols, aluminum hydroxide and ferric hydroxide, are positive in charge while silicic acid is negative. It is well known that a positive colloid

will precipitate a negative colloid when it is mixed with it in the proper proportion. Biltz[3] investigated the mutual action of a number of positive and negative sols and found that there was always a certain concentration which produced optimum precipitation and that either a narrower or a wider ratio led to increased stability. The results were greatly influenced by the manner of mixing. Splichal[55] studied mixtures of silicic acid and aluminum hydroxide and found that they precipitated each other. Even when the colloidal particles failed to precipitate out, the viscosity and opalesence were evidences of incipient coagulation. The precipitation was most rapid when the concentration ratios were one part Al_2O_3 to three parts SiO_2.

The influence of the rate of mixing of the sols to be used in this study was noted. Sols containing 1 gram of the ignited oxides per liter were prepared. Ferric hydroxide and aluminum hydroxide were mixed in the same proportion that they were found in the emulsoid. Since they are both positive the mixture was quite stable. The required amounts of the colloidal silicic acid were measured into a second series of beakers, then the proper amounts of the ferric-aluminum hydroxide mixture were added at different rates. Dropwise additions resulted in almost immediate, complete flocculation. Pouring the silicic acid sol into the iron and aluminum led to the same result. If a slight amount of dilute (N/100) hydrochloric acid was added to the silicic acid before the mixing of the sols, the resulting mixture showed no sedimentation after 24 hours. When the sols were poured together as rapidly as possible, a rather stable sol resulted, although on prolonged standing a slight amount of sediment appeared. This experiment shows then that colloidal SiO_2, Al_2O_3, and Fe_2O_3 may be mixed in the proportions in which they are found in the emulsoid with the formation of a rather stable sol which resembles the natural colloid very much in appearance in low concentrations. The order of mixing has no important effect, while the addition of small amounts of acid stabilizes the mixture. The mixing should be as rapid and as thorough as possible.

VELOCITY OF MIGRATION OF SOLS IN AN ELECTRIC FIELD

Review of Literature.—All workers seem to have found that natural clays regardless of source migrate toward the anode. Aluminum hydroxide is positive. Ferric hydroxide as ordinarily prepared is positive but Powis[47] has shown that a negative sol might be prepared by allowing $FeCl_3$ to run into an excess of dilute NaOH with constant shaking. Silicic acid is ordinarily negative but Billiter[8] found cataphoresis to the cathode at high hydrogen ion concentrations. Billiter studied also the migration of a mixture of sols and concluded that when two colloids of opposite sign are mixed with one in excess, the direction of migration of the whole was always the same as that of the colloid in excess.

Two methods have been used for measuring the velocity of colloidal particles; the U-tube method developed by Nernst, Whetham and Hardy[28] and perhaps most used by Burton[13] and the ultramicroscopic method of observing the velocity of single particles developed by Cotton and Mouton[18], Ellis[22] and Svedberg.[57] Svedberg and Anderson[57] discuss the advantages and disadvantages of each method and are inclined to favor the ultramicroscopic method. Burton[3] regards the U-tube method as the more reliable. The U-tube method was adopted for the present study because of its much greater simplicity.

Experimental.—*Method used.*—The apparatus used was the type recommended by Hatschek[29] for exact work. It consisted of a U-tube provided with two large cocks at the junction of the straight limbs with the bend. An inlet tube, 4 mm. in diameter, equipped with a stop-cock, leads into the lowest point of the latter and was bent at right angles to the plane of the U-tube, terminating in a charging funnel slightly above the tops of the U-tube arms. A scale of millimeters was etched on the limbs. Cylinders of platinum foil, mounted on a strip of ebonite served as electrodes. This strip was provided with terminals and served also as a distance piece.

In filling the tube both cocks in the U-tube were opened and the sol to be measured was allowed to flow in from the charging funnel until it reached the level of the top of the bore in the stopcock. The charging cock was closed first, followed by the remaining two. An equal quantity of distilled water (10 c.c.) was then added to each arm from the top by means of a pipette. The U-tube cocks were then opened and the charging cock turned so that the

sol entered very slowly. Sol was admitted until the electrodes were covered with distilled water. There was always about 7 cm. of distilled water between the electrode and the surface of the sol. Direct current was supplied by a direct current generator operated by an alternating current motor. The voltage, measured by a 125-volt Weston voltmeter, was fairly constant at about 120 volts. The distance between the electrodes was calculated by the method recommended by Hatschek[29]. Twice the length of the straight limb from the lower edge of the electrode was added to half the arithmetical mean of the internal and external circumference of the bend, this value being taken as approximately correct.

Sources of error.—An important error with the U-tube method may be introduced by using water with a specific conductivity very different from the sol. Hardy[28] overcame this by allowing the sol and water to come to osmotic equilibrium in a dialyzing bag before making a determination. Other workers[62] determine the conductivity of the sol and bring that of the water to be used to a corresponding value by the addition of a suitable electrolyte. The electrolyte content of the sols to be studied was so small as to be negligible, therefore, pure distilled water was used. Somewhat more consistent results were obtained however by preparing the tube for a run, then allowing it to stand over night.

Cataphoresis measurements are affected appreciably by changes in temperature, so all exact measurements were made in a small Freas thermostat at 25° sensitive to 0.02°.

If the current is allowed to pass for a long period, the products of electrolysis accumulate and alter by adsorption the velocity of the colloidal particles. This error may be minimized by (1) cutting down the length of the run, and by (2) using sufficient distilled water above the sol surface, thus lengthening the distance between the electrode and the sol.

Results obtained.—In the following studies the current was applied for 5 minutes then reversed for 5 minutes in order to flatten out the menisci. The level of the menisci was then read, the current passed for 20 minutes, and the displacement in both arms noted. The distance between the electrodes was 43.1 cm. and the voltage at the terminals was 120 making the potential gradient 120/43.1 or 2.78 volts per cm. Data from a large number of determinations are summarized in Table 4. The velocity per unit gradient in cm./sec., is given in the sixth column. The potential difference between the Hemholtz double layers of the particles as calculated

by the formula of Lamb[42] is given in the last column. This formula is

$$\text{P. D.} = \frac{4\pi \text{ NV } (300)^2}{\text{K X}}$$

where P. D. = Potential difference in volts.
V = velocity of migration in cm. per sec. under a potential gradient of X units per cm.
N = Viscosity of dispersion medium (in this case H_2O at 25°—10.2×10^3).
K = Dielectric constant of the dispersion medium (K of H_2O=80).
X = Potential drop in volts per cm.
$(300)^2$ = Factor for converting E. S. U. to V.

TABLE 4.—CATAPHORESIS OF 0.1% SOLS AT 25°, UNDER A POTENTIAL GRADIENT OF 2.78 VOLTS PER CM. IN 20 MINUTES.

Sol	Direction of Migration	Movement in		Average	Velocity per unit gradient x10-5	P. D. in volts calcu.
		Anode	Cathode			
Natural emulsoid	To anode	6.0 mm	8.0 mm	7.mm		
	To anode	6.0	8.5	7.25		
	To anode	6.5	8.0	7.25		
	To anode	6.0	9.0	7.50		
			average	7.25 mm	21.8	—.031
SiO_2 (Av.)	To anode	7.0	7.0	7.0	20.9	—.030
Fe_2O_3 (Av.)	To cathode	7.0	7.0	7.0	20.9	+.030
Al_2O_3 (Av.)	To cathode	14.5	16.5	15.5	46.5	+.067
Synthetic (Av.)	To cathode	8.0	11.0	9.5	28.5	+.041

Discussion of results.—The four different determinations of the migration velocity of the natural emulsoid show the variations typical of successive determinations. It is to be noted that the upward movement in the anode is in nearly every case about 2 mm. less than the downward movement in the cathode. This phenomenon has been noted by nearly every investigator who has used the U-tube method. Burton[14] refers to it as a "settling of the colloid". He claims that this settling is due to gravity and that it is uniform in both arms so that while it is added to the velocity in

the one arm, it is substracted from the velocity in the other. For that reason the average of the two would be free from this error.

While Burton's hypothesis seems to explain the fact that the downward movement is more rapid than the upward movement, such as was observed with the natural emulsoid, it is rather difficult to see how it could be applied to the case of the aluminum hydroxide and the synthetic mixture in both of which the upward movement (in the cathode) is higher than the downward movement. Thomas and Foster[62] have recently reported results in which the downward displacement in one arm was 5 to 10 times as great as the upward displacement in the case of certain concentrations of ferric hydroxide sols.

The most surprising fact brought out in the above table is that the synthetic mixture has a positive charge. Since it was made up of about 60% silicic acid which is negative and only 40% of the positive colloids ferric and aluminum hydroxides, it would be expected, according to Billiter's results[8] that a slight migration to the anode would occur. The reason for the movement to the cathode instead may possibly be explained by the strength of the electric charges of the double layers of the separate constituents. The values for the natural emulsoid and silicic acid are about alike and both negative. The value for the ferric hydroxide is identical with that obtained for the above sols, but the direction of migration is opposite. The value obtained for aluminum hydroxide is, however, over twice as large as any of the others. If we multiply the percentage composition of the synthetic sol by the potential differences found for each constituent and then find the algebraic sum of the separate potential differences, the result will be found to have a positive sign.

COMPOSITION OF SYNTHETIC SOL (H_2O FREE BASIS)		P. D.
SiO	59.1% x (—.030)	= —1.773
Al_2O_3	31.9% x (+.067)	= +2.137
Fe_2O_3	9.1% x (+.030)	= + .273
		+ .637

While the method of calculation used is presented only as a rough approximation, it yields results which offer a very logical explanation of the observed facts. The synthetic mixture has the sign of the constituents present in the minimum, because the potential difference of these constituents is enough greater than the

potential difference of the constituent in excess, to more than offset the slight excess in quantity of the latter.

Biltz[9] found that certain positive colloids were always much more effective in precipitating negative colloids than others. Aluminum hydroxide was the most effective sol used. Bancroft[8] explains the superiority of the aluminum by the assumption that alumina is more highly adsorbed than the others. The above data shows that the potential differences of the reacting sols is a factor that can not be neglected.

All the particles of the synthetic mixture in the cathode did not move upward. At the end of the run a secondary meniscus was always noted which was not appreciably moved by the current. In most cases it was about one mm. lower than it was at the beginning of the experiment, which suggests the "settling effect" of Burton. This secondary meniscus is characterized by a density greater than the active meniscus. If size does not affect the velocity of colloidal particles in an electrical field so long as they are so small as to be unaffected by gravity alone, as is claimed by Taylor[60] this difference in rate must be due to a difference in the charges on the particles. The particles in the cathode which show no upward movement must be electrically neutral. In the anode, however, all particles seem to move at the same rate, for there is no indication of a secondary meniscus. This may be due to the ability of the charged particles to drag the neutral particles along with them when working with gravity and a corresponding inability to do so when opposing gravity. There was no visible evidence of electrolytic disturbances. The existence of a considerable proportion of electrically neutral particles in the synthetic mixture would also help to account for the fact that the velocity of the active particles is greater than we would expect if all of the particles had the same charge. For according to the algebraic sum of the potential differences presented above, we would expect the synthetic mixture to be only feebly positive if there were an equal distribution of the potential among all particles. The experimental determination shows, however, that the active particles of this sol have a greater potential difference than any of the constituent sols except the aluminum hydroxide. It appears then that when the positive and negative sols are mixed there is not an equal distribution of the charges, but instead there results the formation of a large proportion of electrically neutral particles, the excess of potential being concentrated on the remaining fraction. If the synthetic mixture contained a large number of neutral particles we

would expect it to be rather unstable. That such is the case is shown by the fact that a considerable portion of it does settle out on prolonged standing unless a peptizing agent is added. Precipitation has been effected in a few instances by mere rapid shaking. Additional evidence is found in the flocculation studies. Only a trace of a strongly flocculating anion is necessary to completely flocculate the synthetic mixture. While the potential difference of the active fraction would lead us to expect that its electrolyte requirement should be over half that of $Al(OH)_3$ it is actually found to be less than one-tenth as large with NaOH.

Effect of the Hydrogen Ion Concentration on the Cataphoresis of the Sols.—*Review of Literature.*—Billiter[8] found that colloidal silicic acid migrated to the anode in alkaline and slightly acid solutions and to the cathode in strongly acid solutions. Hardy[28] found that the specific velocity of globulin was higher in acids than in alkalis and that the weak acids such as acetic and phosphoric had abnormally high values. The specific velocity of the acetic acid globulin was constant over a wide range of concentration of both the acid and the globulin. Burton[13] studied the effect of several electrolytes upon the mobilities of Bredig's silver, gold, and copper sols and found that polyvalent ions of sign opposite that of the colloids caused, in low concentration, a decrease in the migration velocity; still larger quantities brought about a change in the sign of the colloid and slightly larger concentrations caused an increase in velocity of the opposite movement.

Coward[19] working with arsenious sulfide found no reversal of charge with increased acidity at or even subsequent to the addition of enough acid to cause coagulation. There was simply an approach to a minimum mean charge. Powis[47] was able to reverse the charge ordinarily found on colloidal ferric hydroxide by allowing a ferric chloride solution to slowly mix with a dilute solution of NaOH with constant shaking. Loeb[39] has shown that gelatine is isoelectric at a pH of 4.7, that lower values yield a positive sol while higher values yield a negative sol.

These results show that it is possible to reverse the sign of certain sols by the addition of the proper quantity of an appropriate electrolyte.

It was found in the cataphoresis experiments reported above that the synthetic sol was positive while the natural colloid was negative. The effect of the additions of varying quantities of dilute acid and alkali on the mobilities of each of the sols was

studied in order to see if the direction of migration could be reversed.

Experimental.—The method used for these studies was the same as that described above except that the measurements were made at room temperature. The fluctuation in the course of a series of determinations was never large. Since only comparative values were desired no attempt was made to adjust the conductivity of the supernatant water to that of the sol. The current was not reversed at the beginning of the run; instead, readings were taken at frequent intervals in order to observe any change in the rate of migration, which might be induced by electrolytic disturbances.

Effect of HCl and NaOH upon the mobility of the natural emulsoid.—Four, six, and ten c.c. of .01N HCl were added to 100 c.c of a 0.2% emulsoid sol and 4, 6, 10 and 20 c.c. .01N NaOH respectively to a second series of the same sol and the migration velocity determined as soon as possible after mixing. The data from these determinations is plotted on the curves in Fig. 4. The movements in the anode are designated by a + sign, in the cathode by a — sign. The no-treatment curves show in the first 20-minute interval the same variation noted above in the 20-minute runs. The migration downward is slightly more rapid than the migration upward. The migration in the cathode is very uniform throughout the whole course of the experiment, while the upward migration in the anode is retarded more and more with time. When a drop of bromthymol blue was added to the water in the anode, at the end of the run it was changed to its full acid color; the water in the cathode yielded an alkaline reaction of a like intensity. The most logical explanation of the retardation of the migration in the anode is that the upward moving negative colloid comes in contact with the positive hydrogen ions after the experiment has run for 30 minutes and its negative charge is reduced thereby. The migration in the cathode shows no change in the duration of the experiment, because the colloid and the accumulating hydroxyl ions are moving in the same direction, and consequently will not come in contact as quickly as the hydrogen ion and the sol in the anode which are always moving toward each other.

Small additions of dilute acid reduce the mobility and slightly larger amounts render the sol isoelectric and rapid flocculation results. The addition of acid in larger quantities fails to reverse the sign on the particles. The rapid downward movement observed with the addition of 6 c.c. .01N HCl after 28 minutes is due largely

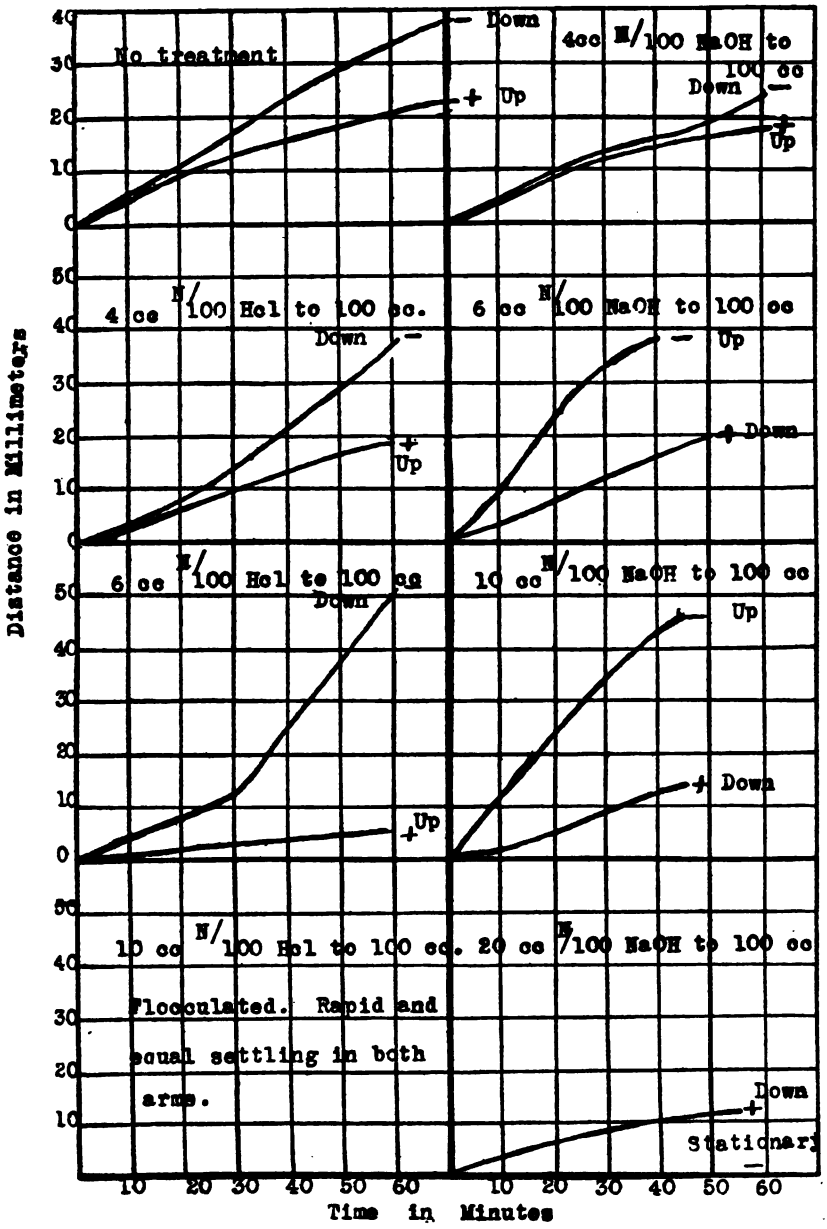

Fig. 4.—Effect of Reaction upon the Mobility of the Natural Emulsoid.

to gravity. The sol was flocculated at this point and settled rapidly. Small additions of dilute NaOH cause an increase in mobility, larger quantities (20 c.c. .01N) a decrease. The abnormal upward movement shown in the curve is probably an electrolytic disturbance. In each of these cases the larger part of the sol showed practically no upward movement. The readings plotted are the values for the less dense meniscus. In all concentrations plotted this meniscus was very distinct. In the case of the addition of 20 c.c. of .01N NaOH no distinct secondary meniscus was observed, though there was a very faint turbidity, indicating that a few particles had been attracted toward the electrode.

An attempt was made to equalize the conductivity of the supernatant water, and the sols receiving the different treatments by adding the same proportion of the electrolyte to the former that was used in the latter. The U-tube was then filled and allowed to stand for twenty-four hours before the current was applied, in order to establish a better equilibrium at the meniscus. These determinations were made at 25° ± .01°. Current was applied 5 minutes, reversed, then applied 20 minutes. The values given in Table 5 are for the migrations in each arm for the 20 minute period.

TABLE 5.—EFFECT OF REACTION UPON THE CATAPHORESIS OF THE NATURAL EMULSOID.

Treatment	Movement in Anode up	Cathode down	Average
100 c.c. .1% sol + 2 c.c. .01 N HCl	4.0 mm.	7.50 mm.	5.75 mm.
100 c.c. .1% sol + 4 c.c. .01 N HCl	Flocculated.		
100 c.c. .1% sol + 2 c.c. .01 N NaOH	14.0 mm.	9.0 mm.	11.5 mm.
100 c.c. .1% sol + 6 c.c. .01 N NaOH	13.0 mm.	5.0 mm.	9.0 mm.
100 c.c. .1% sol + 10 N NaOH	0.0 mm.	6.0 mm.	3.0 mm.
No treatment	6.5 mm.	8.0 mm.	7.2 mm.

This experiment shows the same changes due to reaction that were noted above. It is to be observed that the more rapid movement is downward with the untreated sol and the acid treatment and upward with the alkali treatment.

Silicic acid.—The data for silicic acid show responses similar to those observed for the natural emulsoid. It was possible however to use much higher concentrations of both acid and alkali, since

flocculation did not result when as much as 50 c.c. of .2 N HCL and .2 N NaOH were mixed with 50 c.c. of a .2% sol. The high acidity did not cause a reversal of charge as was noted by Billiter[8]. The migrations obtained in 20 minutes are given in Table 6.

TABLE 6.—EFFECT OF REACTION ON THE CATAPHORESIS OF SILICIC ACID.

Treatment	Movement in		Average
	Anode up	Cathode down	
100 c.c. .1% sol — no treatment	7.0 mm.	7.0 mm.	7.0
100 c.c. .1% sol + 10 c.c. .01 N HCl	2.5	6.0	4.2
50 c.c. .2% sol + 50 c.c. .20 N HCl	0.0	0.0	0.0
50 c.c. .2% sol + 50 c.c. .20 N NaOH	0.0	0.0	0.0

Ferric Hydroxide.—In preparing the alkaline series for the cataphoresis studies it was observed that 2 c.c. of .01 N NaOH was sufficient to cause an immediate flocculation of 100 c.c. of the .1% sol, while 6 c.c. and 10 c.c. gave a rather stable sol. The direction of migration of the latter two was determined immediately and found in both cases to be toward the cathode. These sols showed a tendency to settle on prolonged standing. Acids caused the same changes in cataphoresis that were noted in the case of the silicic acid and the natural emulsoid treated with alkalis. Small additions caused the formation of the faint secondary meniscus which moved upward toward the cathode more rapidly than the untreated sol. Larger treatments still (20 c.c. acid to 100 c.c. of colloid) brought about an apparent electrical neutrality and no movement whatever could be detected. A considerable amount of $Fe(OH)_3$ went into true solution with the higher concentrations of acid.

Aluminum hydroxide.—Very small amounts of alkali flocculated the aluminum sol and larger quantities did not yield a stable sol as in the case of the ferric hydroxide. Acids had the same effects noted with the iron above.

Synthetic sol.—The synthetic sol showed the same reactions due to the treatments as was shown by the aluminum. Flocculation resulted with traces of alkalis. Larger quantities did not yield a stable sol. In the course of some analyses of the synthetic sol in which sufficient N/5 NaOH was added to bring the concentration in the sol up to about N/13, immediate flocculation resulted, but

after digestion on the water bath for an hour a rather stable sol was obtained. It would appear that if the addition of alkali would cause a reversal of the direction of migration, such a reversal should be obtained in this case. When tested it showed no movement whatever. Enough hydrochloric acid was added to 100 c.c of this alkaline sol to bring its pH to 5.5. The resulting sol was fairly stable but showed no migration.

Conclusions to be Drawn from Cataphoresis Studies.—The natural colloid is negative. The addition of increasing quantities of the active H ion reduces the velocity of migration in lower concentrations and renders it electrically neutral. An excess of acid did not cause a reversal in the sign of the charge. The directions of migration of silicic acid and aluminum hydroxide were not reversed by the addition of more than enough hydrogen and hydroxyl ions respectively, to carry them beyond the isoelectric point. The charge on the ferric hydroxide was reversed by the addition of 6 c.c. .0IN NaOH to 100 c.c. of a .1% sol. The synthetic sol showed the same responses to the changes in reaction that were obtained with aluminum hydroxide. The addition of sufficient NaOH, KOH, $Ca(OH)_2$, and $Mg(OH)_2$ to the synthetic sol to bring the content of these metals in the synthetic sol up to that found in the natural sol brought about an immediate flocculation. The adjustment of the pH by means of HCl to the value of the natural colloid failed to peptize the coagulum.

Boiling the coagulum obtained from the synthetic sol with N/13 NaOH resulted in the formation of a stable sol. This sol showed no migration in an electric field either before or after its pH was brought to the value for the natural colloid. The cataphoresis studies indicate that the natural colloid is not a mixture of colloidal silicic acid, aluminum hydroxide, and silicic acid.

BUFFER ACTION OF SOLS

Review of Literature.—It has long been known that nearly all colloidal solutions have a certain buffer action. The exact mechanism of this effect is not very well understood. Henderson[30] was among the first to call attention to the fact that "if there are present in a solution any bodies which tend to absorb any of the constituents of a solution, which can affect the hydrogen ion concentration of a solution these bodies will tend to act as buffers or

will affect the buffer action of the solution".[16] Bovie[10] found that even so inert a substance as charcoal may have a pronounced buffer action.

Hildebrand[31] has studied the titration curves of some salts of aluminum and similar metals in which the buffer action of colloids probably played a role.

Knight[35] called attention to the strong reserve acidity and alkalinity exhibited by a number of acid soils. Stevenson[56] found wide variation in the buffer action of soils. Mucks and clays showed the largest amounts. He considered the buffer action in clays due to aluminosilicates. The reserve acidity was found to be equal to the reserve alkalinity. Swanson[58] found that the amount of $Ca(OH)_2$ required to neutralize an acid soil depended largely upon the amount of colloidal clay present. Johnson[34] found that there was no close correlation between the lime requirement of soils as determined by the Truog and Veitch methods and the hydrogen ion concentration determined electrometrically. This difference is probably due in most cases to differences in the buffer action of the soils.

The literature shows that some soils have a pronounced buffer action. The amount of buffer action is probably largely a function of the content of colloidal material. No report has been found of the comparative buffer values of the various inorganic colloids such as compose the synthetic sol. Titration curves were determined for each of the pure sols and for the natural emulsoids and the synthetic mixture with the hope that such curves might furnish evidence either for or against the identity of the latter two.

Experimental.—*Titration curves obtained by the Gillespie colorimetric method.*—One hundred c.c. of each of the sols was measured into a series of eleven small flasks and 2, 4, 6, 8, and 10 c.c. of .01N HCl and .01 N NaOH respectively, were added to each. Enough distilled water was added to each flask to bring up the total volume to the constant value 110 c.c. After standing for 5 days the pH of each solution was determined colorimetrically by the method of Gillespie[25]. The values could not be read for the unprecipitated ferric hydroxide solutions because of the intensity of the color of the latter. Wherever possible the values were determined by more than one indicator. In most cases a fair check was obtained; in a few cases, however, a considerable discrepancy was found. These erratic values were obtained with methyl red

and bromphenol blue. The values secured with each of these indicators on a number of different samples are shown in the following table.

TABLE 7.—DISCREPANCIES WITH COLORIMETRIC INDICATORS.

Solution	Methyl red	Brom P. blue
	pH	pH
Suspensoid + 6 c.c. HCl	4.9	3.8
Emulsoid + 6 c.c. HCl	4.9	3.8
SiO_2 + 15 c.c. HCl	4.4	3.3
Al_2O_3 + 15 c.c. HCl	4.7	4.7
Al_2O_3 + 20 c.c. HCl	4.7	4.7

The indicators were both tested with a standard buffer solution and were found to check well, which indicates that the color standards and the indicators were in good condition. The fact that both check on the aluminum hydroxide sol is additional evidence that the error is not due to faulty technique but that it is probably due to some specific reaction between some of the colloidal solutions and the indicators.

When compared on the same soil solution with bromcresol purple the values with methyl red were almost invariably lower. Since the values with methyl red are higher on the acid side than with bromphenol blue and lower on the more alkaline side than with bromcresol purple, the discrepancy is probably due to a reduction in the color of the methyl red by the soil extract. Robbins[51] has also noted discrepancies with methyl red when working with soils.

The curves obtained show some interesting relationships. Aluminum hydroxide has by far the strongest buffer action. The synthetic sol ranks second; this may be ascribed to the fact that it contains about 32% Al_2O_3. Silica also shows considerable buffer effect. With the natural emulsoid and suspensoid a much wider range in pH values is obtained. The relationship may be seen more clearly still by comparing the total changes in pH brought about in the different sols by the addition of equal quantities of acid and alkali.

TABLE 8.—TOTAL CHANGE IN pH WITH 10 c.c. .01N HCl AND 10 c.c. .01N NaOH.

Sol	Highest pH value	Lowest pH value	Difference pH
Aluminum hydroxide	7.7	6.3	1.4
Synthetic sol	7.1	4.7	2.4
Silicic acid	8.6	5.9	2.7
Natural emulsoid	8.7	3.1	5.6

Titration curves determined electrometrically.—The discrepancies noticed with the colorimetric method led to the determination of the curves with the hydrogen electrode. The sols used for these studies were standardized to contain 1 g. of oven dry matter per liter. The studies reported above with the colorimetric method were made on sols containing 1 g. per liter of ignited matter. This makes the solution used for the electrometric determinations considerably more dilute than those used for the colorimetric work, consequently less buffer action is to be expected.

Two, six, ten and twenty c.c. of .01N HCl and .01N NaOH respectively were added to 100 c.c. of each of the sols and after thorough mixing, the stoppered flasks were allowed to stand over night. The hydrogen ion concentration was then determined with the regular Leeds and Northrup Type K apparatus which was carefully tested before, and at frequent intervals during and after making any series of determinations, with a carefully prepared .05 M potassium acid phthalate buffer solution. The values obtained with 20 c.c. of HCl are given in the first column of Table 9. Four days later the values for three of the sols were redetermined and a considerable change was noticed in some solutions. Since the values were found to be changing they were measured again on the 6th and 8th days. No appreciable change was noted for the last two days so all sols were considered to have practically reached equilibrium.

TABLE 9.—CHANGE OF pH ON STANDING 20 c.c. OF .01 N HCl ADDED TO 100 c.c. OF EACH SOL.

Solution	1 day pH	4 days pH	6 days pH	8 days pH
Natural emulsoid	2.90		2.87	2.86
Synthetic sol	2.48	3.28	3.55	3.73
Aluminum hydroxide	2.56	3.92	4.02	4.09
Silicic acid	2.18	2.16	2.20	2.20
Suspensoid	2.19		2.19	2.21

The natural emulsoid, suspensoid, and silicic acid seem to have reached equilibrium in one day with hydrochloric acid. With the aluminum hydroxide and the synthetic sol, complete equilibrium was not obtained even after six days. This time factor could probably be reduced considerably by shaking or heating.

Knight[35] likewise found it necessary to consider the time factor in making titration curves of soils. Hardy[28] pointed out that the absence of transition points in the curves of colloidal solutions was probably merely an expression of the inertia of the colloidal system due to the presence of electrified surfaces and to the large molecules involved.

The sensitiveness of the hydrogen electrode was found to be much less in the colloidal solutions than in true solutions. With the pure colloid the voltage obtained always varied rather widely, as much as 10 millivolts variation being noted with successive readings of the same sol. After the addition of either acid or base, the readings could easily be checked to 1 millivolt after equilibrium had been established. The hydrogen electrode could not be used with the portions of $Fe(OH)_3$ receiving the larger quantity of HCl, for enough of the iron was in true solution to destroy it. This could be easily detected by the rapid fall of potential after shaking was stopped. The final values obtained by the electrometric method are presented in Table 10 and graphically in Fig 5. While the buffer action exhibited is not so strong as indicated in the colorimetric curves, which is perhaps due largely to the difference in concentration pointed out above, the general trend of the curves is the same. Aluminum hydroxide and the synthetic sol have a much stronger buffer action than any of the others.

TABLE 10.—BUFFER ACTION OF SOLS. DETERMINED ELECTROMETRICALLY.

Solution	Treatment							Total Change in pH
	HCl			None	NaOH			
	10 c.c.	6 c.c.	2 c.c.	O	2 c.c.	6 c.c.	10 c.c.	
Natural emulsoid	3.12	3.46		5.04	6.25	6.98	7.89	4.77
Synthetic sol	4.44	4.56	4.80	6.24	6.46	7.08	7.49	3.05
Aluminum hydroxide	4.50	4.73	5.09	5.43	5.76	6.44	7.07	2.57
Silicic acid	3.46	3.62	4.70	5.92	6.96		7.86	4.40
Ferric hydroxide	3.93	4.26	5.15	6.02	6.90	7.47	8.30	4.37
Suspensoid	3.21	3.46	3.98	5.04	6.85		7.56	4.35

Conclusions to be Drawn from the Studies of the Buffer Action.—The titration curves furnish two points of evidence that the chemical combinations existing in the natural and the synthetic sols are not the same. (1) When treated with hydrochloric acid

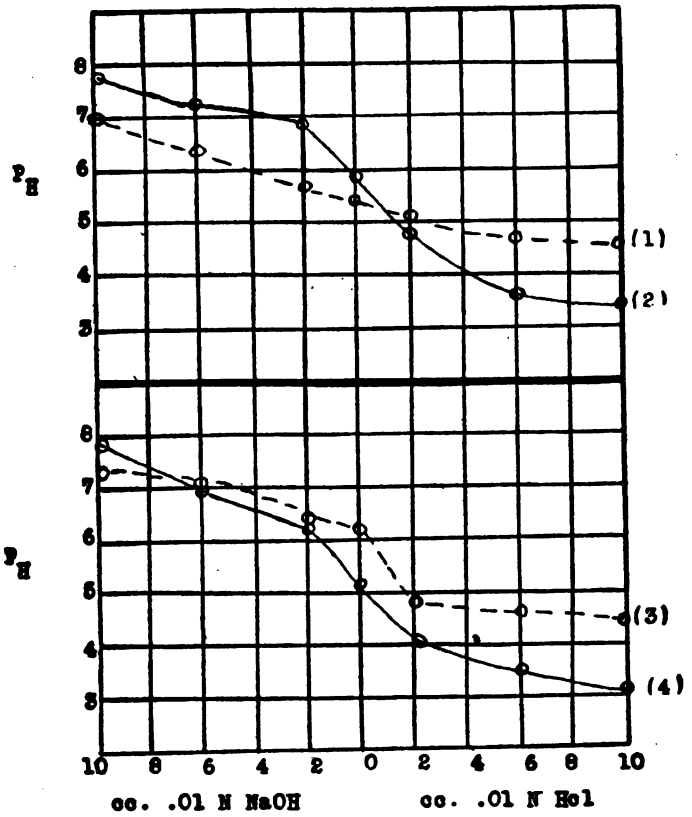

Fig. 5.—Electrometric Titration Curves.—(1) Aluminum hydroxide, (2) Silicic acid, (3) Synthetic sol, (4) Natural emulsoid.

the natural sol reached a constant pH value within a day while the synthetic sol had not reached the point of complete equilibrium after six days. (2) The buffer action of the synthetic sol is much greater than that of the natural emulsoid.

STUDIES ON COAGULATION

Review of Literature.— *Principles involved.*—One of the most peculiar properties of colloidal solutions is that in most cases

mere traces of certain electrolytes are sufficient to cause an agglomeration of the particles into aggregates so large that they will no longer remain in suspension. This is due, theoretically at least, to the neutralization of the charge on the colloidal particle by the ion of opposite charge furnished by the electrolyte.

The principal factors influencing the coagulating power of an electrolyte are according to Weiser[66] as follows: (1) the valence of the precipitating ion; (2) the degree of ionization of the precipitating ion; (3) the tendency of the electrolyte to hydrolyze; (4) the mobility of the ion which frequently decreases with increasing dilution because of increased hydration; (5) the stabilizing influence of the ion having the same charge as the colloid; (6) the velocity of coagulation; (7) the method of adding the electrolyte.

Usually ions with the higher valences are better flocculants than those with lower valences, but this is not always true. In many cases the action seems to be specific. If the ion having the same charge as the colloid is strongly adsorbed by the colloid it will have a tendency to increase its charge, consequently increasing the quantity of the other ion necessary for precipitation. If an electrolyte is added to a colloidal solution very slowly, the amount required for precipitation will be found to be much larger than if it were added at once. This phenomenon is termed acclimatization. Weiser[67] has recently shown that this is not strictly speaking an acclimatization, but is due to the fact that as the electrolyte is added slowly a certain amount of the particles are neutralized. They are not agglomerated sufficiently to settle immediately and when the electrolyte is added a certain amount of it is adsorbed by these electrically neutral particles. If enough electrolyte to neutralize all of the colloid is added at once, under conditions favoring the most rapid and thorough mixing of the two, the amount of adsorption by electrically neutral particles will be kept at a minimum. Measurement of the minimum electrolyte requirement of a colloid should be made only under such conditions. Doubtless, the failure to do so is responsible for many of the variations in the work of different investigators. Another factor is that the different batches of a colloidal solution will differ widely in the amount of electrolyte present at the start. This of course influences the amount required for flocculation of the electrolyte under study.

Burton and Bishop[15] have recently found that the concentra-

tion of the colloid may affect the minimum electrolyte requirements of different electrolytes in even opposite directions. With sols of As_2S_3, Cu and mastic the quantity of univalent ions necessary for coagulation varied inversely with the concentration of the sols: divalent ions were scarcely affected, while trivalent ions varied directly with the concentration of the colloid.

Non-precipitation zones.—Attention was called above to the work of Burton[18] in which a change in the sign of the charge of silver sols was obtained when an excess of $Al_2(SO_4)_3$ was added. His results on flocculation show that if a slight excess of $Al_2(SO_4)_3$ over that required for complete flocculation were added that a rather stable colloid resulted. When a greater excess was added flocculation again resulted. The first precipitation took place as the colloid came to the isoelectric point. Further addition of electrolyte converted it into a sol with a charge opposite to that which it had at first. The second precipitation marks the point where this positive sol was brought to the isoelectric point by the anion.

Weiser[66] passed through a zone of non-precipitation in his studies with HCl on Fe_2O_3, 12 c.c. of normal HCl gave no precipitate after standing several days while either a larger or a smaller amount caused flocculation. A cataphoresis study showed that there was in this case no change in the sign of the colloid. Weiser's explanation is that there is a difference in the adsorption isotherms of Fe_2O_3 for H and Cl ions. It is possible that these isotherms may coincide at some point. At such a point they would neutralize each other and the colloid would be just as stable as if they were absent. If the adsorption isotherms crossed each other we would get a change in the sign of the colloid such as was noted by Burton.

Flocculation of Soils—Results reported on the flocculation of soils vary widely. Hall and Morrison[27] found that free acids were the most powerful flocculants for kaolin. Al was more efficient than Na, but there was no evidence of the valence relation of Linder and Picton and of Whetham. Hydroxyl ions have a negative effect which is able to overcome the positive action of Na, K and NH_4 but is not equal to the greater positive action of the Ca or Ba ions. They felt that the natant condition was due to the presence of free alkaline hydrates and that flocculation ensued as soon as these were neutralized.

Maschaupt[40] and Rholand[50] carried on an extensive contro-

versy as to the part played by the hydroxyl ion in the flocculation of clay by Ca $(OH)_2$. Rholand claimed that flocculation was due to the hydroxyl ion. Maschaupt claimed that it was due to the Ca ion. He showed that NaOH and Na_2CO_3 have a flocculating effect in high concentrations and a stabilizing effect in low concentrations.

Czermak[20] found that frost, heat and salts caused a decrease in soil surface through the coagulation of the soil colloids.

Wolkoff[68] compared the electrolyte requirements of several different soil suspensions. With the best coagulants, $Pb(NO_3)_2$ $Pb(C_2H_3O_2)_2$, $Hg(NO_3)_2$ and to some extent $Fe_2(SO_4)_3$ and $AlK(SO_4)_2$, the minimum requirements are similar for all the soils, but with others the variation is great. Muck is the most resistant of all the classes of colloidal material tested. Wolkoff felt that the flocculating action followed the law of mass action. Schulze's valence law did not hold.

Comber[17] found that silt and clay varied widely in their electrolyte requirements, silt was flocculated most readily in a neutral medium, clay in a slightly alkaline medium. As SiO_2 is known to be coagulated most readily in an alkaline medium Comber contends that SiO_2 functions as a protective colloid in his clay separate.

Protective action.—It has long been known that the electrolyte requirement of a colloid may be materially raised by the presence of various substances. In such a case the substance is said to exert a protective action.

Ruer[48] found that the silver nitrate test for chlorides failed when made in the presence of a solution of colloidal iron even though a decided excess of Cl could be found by other means.

Wolkoff[68] found that the electrolyte requirement of his soil solutions was very materially increased if a little colloidal humus were present.

Comber[17] found that 0.6 mgm. of colloidal SiO_2 was sufficient to protect 300 mgm. of Fe_2O_3. Smith[54] observed that about 50 parts of SiO_2 per million were sufficient to raise the electrolyte requirement of clay suspension almost 300%. He also found that salts containing bivalent cations, i. e., $CaCl_2$, $CaHCO_3$, $MgSO_4$, $Mg\ HCO_3$ aid in the coagulation by alum; NaCl aided slightly, while NaOH, Na_2CO_3 and Na_2SO_4 retarded the reaction. While Smith found that pure SiO_2 sols were coagulated most readily at a pH of about 9, that both SiO_2 and NaOH exerted a protective ac-

tion against his clay suspension, he does not report the effects of NaOH on the SiO_2 protected clay suspensions. According to Comber we would expect the NaOH to facilitate the precipitation of the SiO_2 protected clay particles. If Comber's contention is true, Smith must have worked with a clay suspension in which SiO_2 did not function as a protective colloid.

Oden[44] studied the protective effect of humus on various clays and found that the action was specific with the clay and the electrolyte used.

Conclusions from the literature.—Murry[42] recently made a thorough review of the work on coagulation of colloids and was unable to find any general expression. The following points, however, seem fairly well established:

(1) The ion of opposite sign to that of the colloid is responsible for the coagulation. The action is specific.

(2) Ions of higher valence are most effective as coagulants.

(3 The ion of the same sign as the colloid has a modifying effect.

(4) Equivalent quantities of different ions are probably entrained by the coagulum.

(5) A minimal concentration of electrolyte must be present before coagulation begins.

(6) The ion originally present in the colloid has an important effect.

Since coagulation is specific with respect to both colloid and electrolyte, the determination of the minimum electrolyte requirements of the natural and the synthetic sols under study, should throw additional light on the question of the similarity or dissimilarity of the chemical combinations existing in each.

Experimental.—*Effect of concentration of sol on the rate of settling.*—A study of the rate of settling of different concentrations of the natural emulsoid with a fixed amount of electrolyte was made in order to find the concentration best suited for the experiments on the minimum electrolyte requirement. Volumes of 98 c.c. of sols containing 2, 1, 0.5, 0.2, 0.1 and 0.04% respectively, were placed in 100-c.c. graduates, 2 c.c. of $N/5H_2SO_4$ was added and the solutions thoroughly mixed by inversion. The volumes of sediment were read at frequent intervals. The rates of settling are plotted in Fig. 6. The 0.1% sol showed the most rapid settling: 0.04% was seen to be completely flocculated immediately, but the floccules formed were so light and fluffy, that they settled very

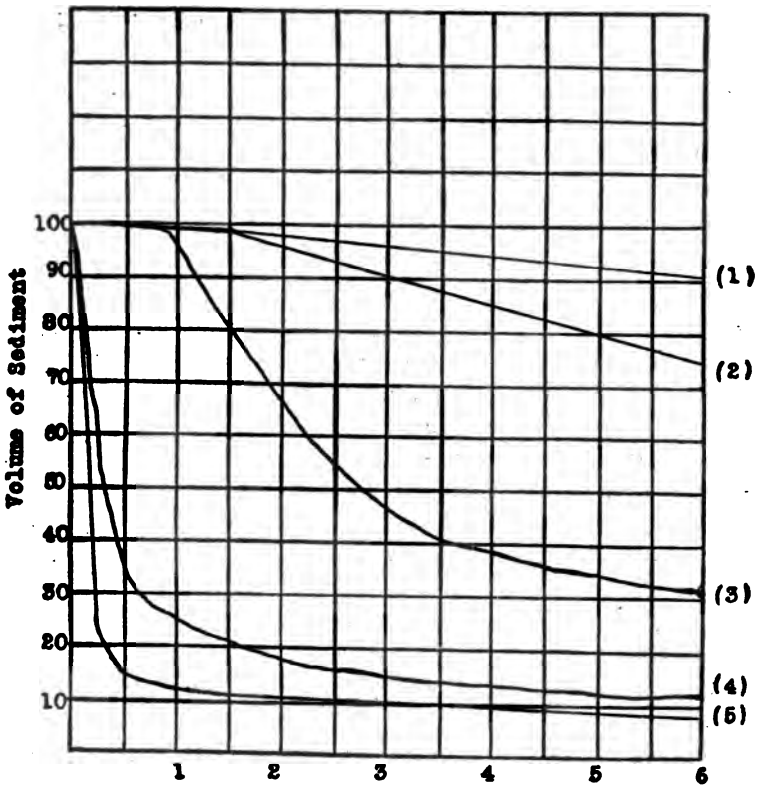

Fig. 6.—Effect of Concentration of the Colloid upon the Rate of Settling after Flocculation.
(1) 2.0 per cent sol, (2) 1 per cent, (3) .5 per cent, (4) .2 per cent, (5) .1 per cent.

slowly, leaving a supernatant liquid that was still somewhat turbid. With the 0.1% sol the meniscus was sharp, the supernatant liquid very clear, and the rate rapid. For these reasons it was adopted as the concentration best suited for studies of the comparative electrolyte requirement.

Comparative electrolyte requirement of 0.1% *sols.*—The minimum electrolyte requirements of each of the sols with several typical electrolytes were determined by the usual "trial and error" method. The results are given in Table 11. The concentrations of electrolyte are expressed in terms of milli-equivalents per liter. They represent the minimum concentrations producing complete flocculation in 24 hours.

While there are several variations that are rather hard to un-

TABLE 11.—ELECTROLYTE REQUIREMENT OF .1% SOLS IN MILLI-EQUIVALENTS PER LITER.

Electrolyte	Emulsoids		Sus.	Al_2O_3	Fe_2O_3	SiO_2
	Syn.	Nat.				
HCl	4.32	0.29	0.29	—	—	———
H_2SO_4	0.29	.23	.23	1.15	1.30	166.6+
NaOH	0.02	46.15	46.15	0.18	0.12	100.0+
$Ca(OH)_2$	0.20	1.67	2.31	0.35	0.14	1.94
KCl	1.19	1.96	2.91	0.89	1.28	500.0+
$Ca(NO_3)_2$	3.92	0.20	0.25	3.92	1.19	100.0+
$Al_2(SO_4)_3$	0.15	0.09	0.07	0.57	0.39	0.29

derstand, the values as a whole are of the nature we would expect from the nature of the charges found in the cataphoresis studies. The natural emulsoid is very sensitive to acids and polyvalent cations, while the synthetic sol is most sensitive to the hydroxyl ion and polyvalent anions. Only 0.02 of a milli-equivalent of NaOH is necessary for flocculation with the synthetic sol, while 46.15 milli-equivalents or over two thousand times as much is required in the case of the natural emulsoid. Silicic acid proved very stable. The minimum requirement was over 100 with all electrolytes studied except $Ca(OH)_2$ and $Al_2(SO_2)_3$. The values for the two soil separates are very closely related throughout. The experiment leaves no doubt but that there is a distinct difference in the chemical combinations existing in the natural and synthetic sol. The electrolyte requirement of the synthetic sol is distinctly lower than the aluminum hydroxide in almost every case, and this strengthens the opinion that it contains a considerable proportion of electrically neutral particles as was indicated in the cataphoresis studies.

Effect of reaction on electrolyte requirement.—Comber's results, cited above, show that his clay separate was flocculated more readily in an alkaline medium. Samples of 0.1% SiO_2 and 0.1% natural emulsoid were rendered alkaline by the addition of 10 c.c. of .01N NaOH to 100 c.c. of the sols. The resulting Sorensen value was about 9.0. Smith[54] reports that silicic acid has a pronounced protective action on clay suspensions. This point was tested also by determining the electrolyte requirement of an emulsoid sol to 100 c.c. of which 10 c.c. of a 0.1% sol of SiO_2 had been added. The results are given in Table 12.

TABLE 12.—EFFECT OF SiO_2 AS A PROTECTIVE AGENT AND OF THE REACTION UPON THE ELECTROLYTE REQUIREMENT OF THE NATURAL EMULSOID AND SiO_2.

Electrolyte	Neutral Series			Alkaline Series pH9		
	SiO	N. Em.	N. Em. +10% SiO_2	SiO_2	N. Em.	N. Em. +SiO_2
$Ca(NO_3)_2$	100+	.20	.29	14.82	.48	.65
$Al_2(SO_4)_3$	.29	.09	.12	.44	.35	.27

While the electrolyte requirement of the SiO_2 was lowered in the alkaline medium, in the case of the $Ca(NO_3)_2$, it was raised slightly with $Al_2(SO_4)_3$. With the natural emulsoid the requirement was raised in every case. The addition of 10% SiO_2 to the emulsoid increased its electrolyte requirement in both the neutral and the alkaline mediums.

Effect of reaction on the rate of settling.—Arrhenius has recently reported[1] that the rate of settling of clay suspensions varied widely with the reaction of the suspension. He obtained curves which resembled those of Loeb for gelatine and he argues for that reason that clay is an ampholyte with an isoelectric point at about pH 4.3. If this is true it is a point of considerable importance. A few simple experiments have been made with the natural emulsoid which indicate that there are at least three points at which settling is more rapid.

The preliminary experiments were made by the method used by Arrhenius. A definite quantity of the emulsoid was placed in a 100-c.c. graduate, the acid or alkali added, and the volume made to 100 c.c. with distilled water. The graduates were then shaken uniformly to ensure thorough mixing. After definite intervals of time the volumes of the sediments were read. While this method indicated that there were certain points of more rapid settling, it was found impossible to duplicate results. As was shown above, the rate of addition of the electrolyte and the thoroughness of mixing play an important role in flocculation studies. In order to secure the greatest possible speed and uniformity of mixing a device made as follows was used: A rubber stopper was selected that would fit tightly in the small end of the ordinary student lamp chimney, a circular groove 2 cm. in diameter, 2 mm. thick and 1 cm. deep was cut in the small end of the stopper. A piece of glass tubing about 17 cm. long and 2 cm. in diameter was fitted

into this groove. The stopper and tube were then placed in the chimney and a little paraffin was poured around the junction of the tubes and stopper. Fifty c.c. of water were placed inside the inner tube and the height of the meniscus marked. In making a series of determinations a definite volume, 50 c.c. of the sol, was placed in the chimney with a pipette, the requisite amount of electrolyte added to the inner tube and its volume made up to the 50-c.c. mark with distilled water. A quick and fairly uniform mixing was obtained by placing a stopper in the open end of the chimney and quickly inverting it. After mixing, the sol was poured into 100 c.c. graduates for settling. A similar device, using two straight glass tubes, was described by Weiser[67]. The lamp chimney gives an advantage over the straight tubes, in that the constriction at the juncture of the smaller end and the base, serves to give a swirling motion to the liquids as they come together, insuring a somewhat better mixing. The size of the chimney is also very convenient.

The experiment on the effect of reaction on the rate of settling of the emulsoid was repeated using this device to ensure uniform mixing and adding 2, 4, 6, 8, 10, 12, 15, 20, 25, 30, 35, 40, 45, and 50 c.c. of .01N HCl and 5, 10, 15, 20, 30, 40 and 50 c.c. of .1N NaOH as electrolytes. The volumes of sediment were read periodically. The data is plotted in Fig 7. This experiment was repeated seven times with HCL and the maximum rates of settling were noted at approximately the same point each time so there can be little doubt but that some significance can be attached to the observations. There are, however, in every case two points of more rapid settling at which either larger or smaller quantities of acid retard the rate of settling. These two points cannot be seen at the same time. If our observation is made one hour after mixing, the maximum settling will be observed with about 30 c.c. of .O1N HCL. After 24 hours, however, the treatments on either side of 30 c.c. will yield about the same volume of sediment. On the other hand, no settling can usually be detected with less than 15 c.c. of HCl after one hour. But after 24 hours the samples receiving in the neighborhood of 5 c.c. will be found to have settled much more rapidly than the samples receiving 8 or 10 c.c. The difference in volume with these concentrations persists for some time. After fifty hours the 10-c.c. tube had over 25% more sediment than the 5-c.c. treatment.

With NaOH the rate of settling is very much slower, consequently no curve was obtained for the one hour period. After 24 hours, however, there was observed a maximum settling point with

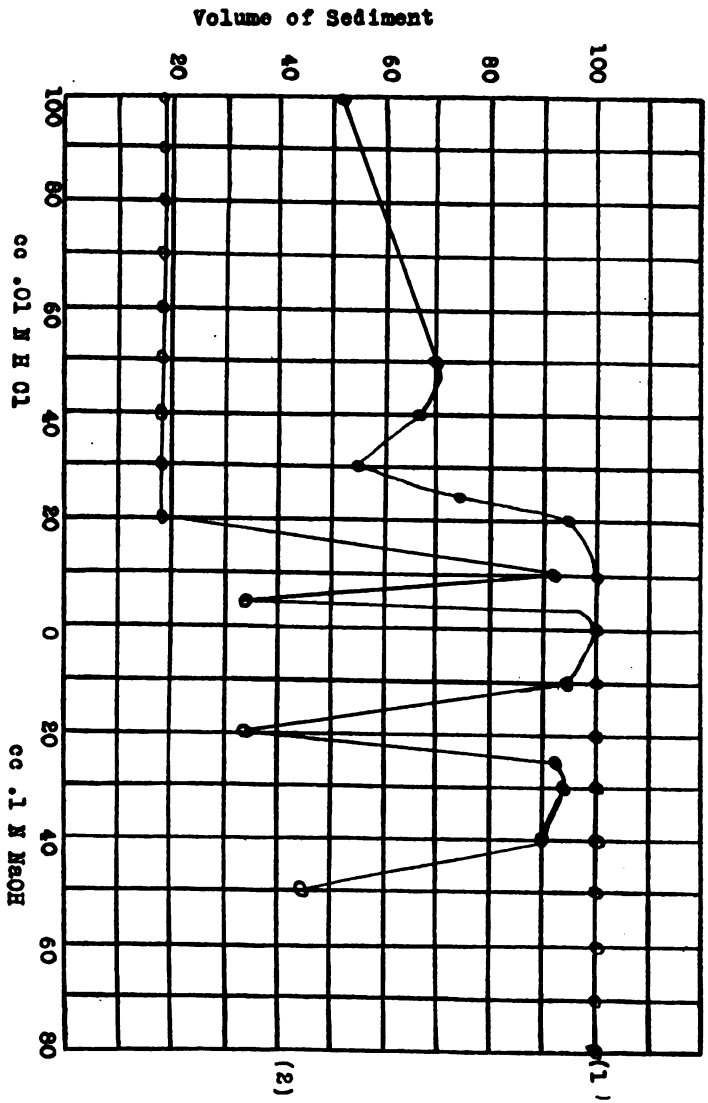

Fig. 7.—Effect of Reaction on the Rate of Settling.
(1) After 1 hour (2) After 24 hours.

20 c.c. of N/10 NaOH. This value has been repeatedly confirmed.

With 10 and 15 c.c. of .1N NaOH there is no visible evidence of flocculation. The solutions appear perfectly clear and homogeneous but after a couple of days a slight settling is noticed at the top, indicating that the degree of dispersion has been decreased.

Results obtained with K_2HPO_4 seem to be similar to those ob-

tained with NaOH. Quantities of K_2HPO_4 equivalent to 25, 30, 35, 40, 45, 50, 55 and 60 c.c. of the N/5 solution were mixed with 50 c.c. of the .2% emulsoid by means of the concentric tube device. After 48 hours the tubes receiving 40, 45, 55, and 60 c.c. were almost completely flocculated, while the tubes receiving 50, 35, 30 and 25 c.c. were perfectly stable even after one week. There seems then to be at least three concentrations of HCl and NaOH which give a more rapid rate of settling than either a slightly larger or a slightly smaller amount. Two of these points have been found on the acid side of neutrality and one on the alkaline side. The Sörensen value of the first acid point is about 5.0; that of the second acid point is beyond the Gillespie colorimetric scale (less than 3.1). The most logical explanation of these facts seems to be that with 10 c.c. and perhaps 40 c.c. of .01 N HCl and with 25 c.c. .1N NaOH and with 50 c.c. of N/5 K_2HPO_4 certain "zones of non-precipitation" have been reached such as almost every worker in the field of colloid chemistry has at some time encountered,* rather than the single isoelectric point which is characteristic of amphoteric substances as claimed by Arrhenius. The Donnan equilibrium is probably responsible in both cases.

Conclusions to be Drawn from the Flocculation Studies.—The synthetic sol and each of the pure constituent sols were flocculated most readily in an alkaline medium while the addition of a small amount of alkali seemed to peptize the natural colloid and a much larger quantity was required for flocculation. On the other hand just a trace of acid was sufficient to flocculate the natural colloid, while the constituent sols and the synthetic sol showed a much higher requirement. Since the action is opposite in both cases the nature of the chemical combinations existing in the synthetic sol must be very different from those existing in the natural sol. The data indicates also that there is very little if any free colloidal SiO_2 in the natural colloid, since colloids protected by SiO_2 seem to be flocculated most readily in an alkaline medium.

COMPARATIVE ANALYSES IN DILUTE SOLVENTS

Review of Literature.—The early work of Bauer, to which attention has already been called, showed that certain soils contained practically all of their iron and aluminum in a form that is soluble in hydrochloric acid. Since that time scores of investigations have been made, and it seems to be quite definitely established,

*Refers to Review of Literature above.

that certain soils in tropical and subtropical countries are made up more or less completely of the broken down end products of weathering of the complex igneous alumino-silicate rocks which formed the parent material. Such soils are known as laterite soil, or *terra rosa*, depending upon the extent of the weathering.

Schloessing[53] made analyses of soils from France and from Madagascar, using dilute NaOH (1.35%) as a solvent. In 17 soils mostly from France, the amount of Al_2O_3 extracted was less than 1%, SiO_2 ran between 1 and 2%. In nearly every case the ratio of SiO_2 to Al_2O_3 was larger than in kaolin indicating the presence of free SiO_2. Five soils from Madagascar showed the following compositions:

	1	2	3	4	5
Al_2O_3	11.7%	8.1	6.59	4.69	11.40
SiO_2	1.61	1.92	5.15	5.05	.94

Schloessing claims that the greater part of the Al_2O_3 in soils 1, 2 an 5 must have been free, while in 3 and 4 it may be largely in the form of a readily decomposable silicate.

Horvath[33] studied the solubility of soils in dilute alkalis and found that the colloidal silicic acid could be extracted by boiling 15 minutes with a 1% solution of Na_2CO_3. Fraps[23] working on Texas soils proposes the use of 4% NH_4OH as a solvent for the determination of the amount of inorganic colloids in soils. This material was made up of from 47.5 to 60% SiO_2, 11 to 24% Fe_2O_3 and from 8.7 to 40% Al_2O_3. The soils containing the higher per cent of soluble colloids were almost invariably high in soluble Al_2O_3.

Experimental.—The solubility of colloidal material in any solvent is greatly influenced by the size of the particles. The particles in the natural emulsoid used in this investigation, as well as those of the synthetic sol, are of a somewhat similar size for they were thrown out of suspension by the same centrifugal force. Since they are comparatively uniform in the amount of surface they expose to a dilute solvent, it would appear that if analyses were made of the fractions of each dissolved by different solvents under as near the same conditions as possible, such analyses would throw some light on the nature of the chemical combinations existing in the natural colloid. For we would expect iron, alumina and silica combined in a complex silicate to have solubilities different from a mixture of free silica, iron and alumina having the same ultimate analysis.

Results of Analyses.—With this in mind, analyses have been made of the fractions of the natural and synthetic colloids soluble in different concentrations of HCl and NaOH. Because of the divergence in the H_2O content of the oven dry natural and synthetic sols, the samples were measured on the water free basis, (ignited wt.). Because of the possibility of a change in solubility on drying, the analyses were made on sols, the concentrations of which had been carefully determined by evaporating aliquots to dryness and igniting to constant weight. The usual analytical methods were used. The period of digestion was three hours on the water bath.

TABLE 13.—ANALYSES OF NATURAL AND SYNTHETIC SOLS IN DILUTE HCl AND NaOH.

	1	2	3	4	5	6	7	8
Solvent	SiO_2	Al_2O_3	Fe_2O_3	$\frac{Al_2O_3}{SiO_2}$	$\frac{Fe_2O_3}{Al_2O_3}$	Soluble	Insol. by diff.	Insol. by det.
(1) Total analysis (Calculated to H_2O free basis).								
Natural	59.15	31.92	9.11	1:1.85	1:3.5			
Synthetic	59.15	31.92	9.11	1:1.85	1:3.5			
(2) Con. HCl								
Natural	.21	31.62	9.02		1:3.5	40.85	59.15	59.83
Synthetic	All in true or colloidal solution							
(3) 5% HCl								
Natural	7.34	15.67	3.82		1:4.1	26.83	73.17	73.5
Synthetic	No precipitate							
(4) N/13 HCl								
Natural	7.68	5.80	1.60		1:3.6	15.08	84.92	
Synthetic	Fe_2O_3 and Al_2O_3 apparently in true solution. SiO_2 probably largely colloidal.							
(5) N/13 NaOH								
Natural	9.00	5.12		1:1.76		14.12	85.88	91.24
Synthetic	Rather stable red sol. Almost neutral electrically.							
(6) 1% NaOH								
Natural	13.31	7.56		1:1.76		20.87	79.13	84.2
Synthetic	33.63	21.28		1:1.67		56.91	43.09	49.3

Conclusions to be Drawn from the Analyses.—The differences between the natural and synthetic colloids are marked throughout. In all concentrations of acid, the reddish color of the synthetic sol disappears and it takes on a faint opalescence, all iron ap-

parently going into true solution. With dilute alkali (M/13) the synthetic sol is immediately precipitated, but on digestion on the water bath, it goes into a rather stable colloidal condition. When this sol was subjected to cataphoresis, no migration was apparent. It would seem that here would be the place that a reversal in charge would be expected. With a higher concentration of alkali (1%) all iron is precipitated and part of the Al_2O_3 and SiO_2.

All concentrations of both solvents caused a coagulation of the natural colloid. The coagulum was gelatinous, extremely bulky and almost impossible to filter and wash thoroughly. The samples treated with alkali were much more bulky and gelatinous than those treated with acid. That considerable Na is retained by both the natural and synthetic sols is indicated by the marked difference in the insoluble fractions as determined analytically (column 8) and as calculated by difference (column 7). In the case of 1% NaOH digestion the precipitate was washed two days with distilled water before it was ignited and weighed. It seems probable that at least part of this Na is chemically combined with the aluminum and silica.

Another interesting relationship is seen in the fourth and fifth columns. In the case of the NaOH digestions the higher concentrations of alkali show the larger per cent of material dissolved, as would be expected. If a comparison is made between the relative amounts of Al_2O_3 and SiO_2 extracted in each case it is found that the ratio is the same, that is 1 part of Al_2O_3 to 1.76 parts SiO_2. This ratio does not differ widely from the ratio of these substances shown by the total analysis to be present in the material. This would seem to indicate that the Al_2O_3 and SiO_2 exist in the sol largely in the combined state for if there were much, free Al_2O_3 a narrower ratio would be expected; and if the Al_2O_3 were all combined and there were any appreciable excess of SiO_2 the ratio would be wider. This is indicated by Schloessing's work. If both substances were present in the free state entirely the ratio would be somewhat narrower as is shown by the analyses of the synthetic mixture.

A similar relationship exists in the ratio of Fe_2O_3 to Al_2O_3 dissolved by M/13 HCl from the natural emulsoid. The ratio in this case is 1:3.6 as compared with 1:3.5 obtained in the total analysis.

The analyses then furnished additional evidence that the natural emulsoid is not a mixture of colloidal silica, aluminum and iron but is rather a complex alumino-silicate.

DISCUSSION OF RESULTS

The finest colloid extract obtained from the Putnam subsoil formed when dry a translucent, physically homogeneous, mass. When treated with hot, concentrated hydrochloric acid, all of the iron and aluminum went into true solution. The behavior toward the acid solvent was almost identical with the behavior observed by numerous investigators of tropical laterite in which the iron, aluminum and silicon exist more or less completely as the separate oxides of these elements. In the process of formation all this material exists for a time in the colloidal state.

Because of this similarity in behavior, it was considered possible that the finest colloidal material in the Putnam subsoil might also represent the end products of weathering, whose presence had not been recognized by soil investigators, because it has been masked by the preponderating masses of undecomposed material. It was considered probable that any process which would go to completion in the tropics would take place to a certain extent in temperate regions, but much slower in accordance with Van't Hoff's law.

It was considered probable that if a synthetic mixture of colloidal silicic acid, aluminum hydroxide, and ferric hydroxide, having the same ultimate analysis as the natural colloid, were prepared, and its physico-chemical behavior compared with the natural colloid, that sufficient data might be obtained to prove or disprove the identity of the chemical combinations existing in the two.

Such studies have been made and they show quite conclusively that the natural colloid is not a mixture of colloidal SiO_2, Al_2O_3 and Fe_2O_3. The analyses in dilute solvents indicate that the natural colloid does not contain any appreciable amount of free $Si0_2$ or Al_2O_3 but that it is made up largely of complex aluminosilicates.

In those tropical regions in which the complete breaking down of the complex silicates into the simple oxides occurs, Al_2O_3 and Fe_2O_3 accumlate, while SiO_2 disappears. In a slightly acid medium, sols of Al_2O_3 and Fe_2O_3 are comparatively stable and would be as likely to be lost by leaching as SiO_2. In a slightly alkaline medium, however, Al_2O_3 and Fe_2O_3 are precipitated, while SiO_2 is still stable. Under these conditions, we might expect the accumulation of Fe_2O_3 and Al_2O_3 and the disappearance of SiO_2.

If we resurvey the literature on lateritization in this light, we

find according to Vageler[64] that the process of lateritization takes place only in soils having an alkaline reaction. The presence of humic acids prevents the process. Only in those regions in which the humic acids are completely destroyed during the hot dry period, thus giving the soil an alkaline reaction for a large part of the year, do we find the complete breaking down of the alumino-silicates into the separate sols.

Since laterite soils are very old soils, it is difficult for those accustomed only to the type of weathering found in the humid temperate regions, to understand the alkaline reaction, for in the latter region the alkali and alkali earth metals are the first substances to disappear and an old soil is almost invariably an acid soil.

The explanation seems to be that in the humid temperate regions the weathering process consists more largely of a leaching of bases and a physical disintegration, while in the laterite regions of the tropics, due perhaps largely to the higher temperatures and the lack of humus, an actual chemical decomposition of the alumino-silicates takes place, while there is still present a sufficient amount of bases to give the soil an alkaline reaction.

SUMMARY

(1) A method has been developed for the extraction of colloidal material from soils by means of a high centrifugal force.

(2) The amount of colloidal material that could be readily extracted from an air dry sample of a heavy clay soil was only a small fraction of the amount that could be extracted from samples which still contained the natural water content.

(3) The physical properties of the colloidal material were studied and its chemical composition determined.

(4) All the iron and aluminum in the colloidal material was soluble in concentrated hydrochloric acid.

(5) Preliminary experiments indicated that the natural colloid might be made up of the completely broken down end products of weathering, SiO_2, Al_2O_3, and Fe_2O_3, such as compose the laterite of the tropics. In order to test this hypothesis, a synthetic mixture of colloidal SiO_2, Al_2O_3, and Fe_2O_3, having the same ultimate analysis as the natural colloid, was prepared and some of its physico-chemical properties studied in comparison with studies of the same properties of the natural colloid. The comparative studies included determinations of (a) cataphoresis, (b) buffer ac-

tion, and (c) electrolyte requirement. All data obtained furnished strong evidence that the natural colloid was not made up of a mixture of the colloidal oxides.

(6) Comparative analyses of the portions of the natural and synthetic sols soluble in dilute acid and alkali strengthened the above conclusion and furnished evidence that the natural sol was made up largely, if not completely, of a complex, readily decomposed alumino-silicate.

BIBLIOGRAPHY

1. Arrhenius, Olof. 1922. Clay as an ampholyte. J. Am. Chem. Soc. **44**, 521.
2. Ashley, H. A. 1909. The colloidal matter of clay and its measurement. U. S. Geol. Survey Bul. 388. 1-65.
3. Bancroft, W. D. 1921. Applied Colloid Chemistry p. 266. McGraw-Hill Co., New York.
4. Bauer, Max. 1907. Beitrag zur Kenntnis des Laterites. Neus. Jahr. fur Miner. Festband. S. 33.
5. Beaumont, A. B. 1919. Studies in the reversibility of the colloidal condition of soils. Cornell Ag. Exp. Sta. Memoir 21.
6. Bemmelen, J. W. Van. 1909. Beitrag zur Kenntnis der Eigenschaften der Hydrogels bei ihrer Entwassererung und Weiderwasserung. Ztschr. Anorgan. Chem. **42**: 265-314. 1910, Die Absorption, 196, 214, 232.
7. Billiter, J. 1904. Ber. Wien. Akad. Wiss. 113, 1159. (Cited by Burton p. 169).
8. Billiter, J. 1905. Theorie der Kolloide II. Zeit. Phys. Chem. **51**: 150.
9. Biltz, W. 1904. Ueber die gegenzeitige Beeinflussung colloidal geloster Stoffe. Ber d. D. Chem. Gess. **37**: 1095.
10. Bovie, W. T. 1915. A direct reading potentiometer for measuring and recording both the actual and total reactions of solutions. J. Med. Res. **33**: 925.
11. Bradfield, R. 1922. A centrifugal method of preparing colloidal ferric hydroxide, aluminum hydroxide and silicic acid. J. Am. Chem. Soc. **44**, 965.
12. Bureau of Soils Report. 1912. p. 1730.
13. Burton, E. F. 1916. Physical Properties of Colloidal Solutions. Longmans Green and Co. London.
14. Burton, E. F. 1919. A new method of weighing colloidal particles. Proc. Roy. Soc. London. **95A**: 480.
15. Burton, E. F., Bishop, E. 1920. Coagulation of colloidal solutions by electrolytes. Influence of the concentration of the sol. J. Phy. Chem. **24**: 703.
16. Clark, Wm. M. 1920. The Determination of Hydrogen Ions. Williams and Wilkins. p. 34.
17. Comber, N. M. 1920. The flocculation of soils. J. Ag. Sci. **19**: 425.
18. Cotton, A., Mouton, H. 1904. Etude directe due transport dans le courant des particales ultramicroscopic. Compt. Rendu. **138**: 1584, 1692.
19. Coward, T. A. 1913. New experiments on colloids. Trans. Faraday Soc. **9**: 142.
20. Czermak, W. 1912. Ein Beitrag zur Erkenntnis der Veranderungen der sog. physicalische Bodenigenschaften durch Frost, Hitze and Beigabe einiger Salze. Landw. Vers. Stat. **76**: 75.
21. Edwards, M. G. 1914. Occurence of free alumina in the soils of the United States. Econ. Geol. **9**: 112.
22. Ellis, R. 1911. Die Eigenschaften der Oleemulsionen. Zeit. Phys. Chem. **78**: 321.

23. Fraps, G. S. 1914. Determination of inorganic colloids in soils. Texas Ag. Exp. Sta. Bul. 165.
24. Fry, W. H., Middleton, H. E. Moore, Chas. J. 1921. Determination of colloids in soils. J. Ind. Eng. Chem. 13:527.
25. Gillespie, L. J. 1920. Colorimetric determination of hydrogen ion concentrations without buffer mixtures with special reference to soils. Soil Science 9: 115.
26. Gustafson, A. F. 1922. The effect of drying soils on the water soluble constituents. Soil Science 13: 172.
27. Hall, A. D., Morrison, C. G. 1907. Flocculation of turbid liquids. J. Agr. Sci. 2: 244.
28. Hardy, W. B. 1905. Colloidal solutions. The globulins. Jour. of Physiol. 33: 251.
29. Hatschek, Emil. 1920. Laboratory Manual of Elementary Colloid Chemistry. P. Balkiston's Son and Co. p. 81.
30. Henderson, L. J. 1909. On the neutrality equilibrium in blood and protoplasm. J. Biol. Chem. 7: 29.
31. Hildebrand, J. H. 1913. Some applications of the hydrogen electrode in analysis, research and teaching. J. Am. Chem. Soc. 35: 847.
32. Hilgard, E. W. 1914. Soils. Macmillan Co., N. Y.
33. Horvath, Bela Von, 1916. Uber den Gehalt der Boden an amorpher Kieselsaure. Intern. Mitt. F. Bodenkunde. 6: 288-93.
34. Johnson, H. W. 1922. The relation of hydrogen ion concentration to the lime requirement of soils. Soil Science 13: 7.
35. Knight, H. G. 1920. Investigations of acid soils by means of the hydrogen electrode. J. Ind. Eng. Chem. 12: 457.
36. Kuhn,—. 1853. J. pr. Chem. (1) 59:1. (Cited by Taylor, p. 15.)
37. Lacroix, A. 1914. Les produits d'alteration des roches silicate alumineuse de Madagascar. Compt. Rendu. 159: 617.
38. Lamb, 1888. Phil. Mag. 1888. p. 60.
39. Loeb, J. 1918 Amphoteric colloids. Jour. Gen. Physiol. 1: 39, 237, 353, 483, 559.
40. Mauschaupt, J. G. 1914. Hydroxyl ions and the flocculation of clay suspensions. Landw. Vers. Stat. 83: 467.
41. Mitscherlich, E. A., Floess, R. 1912. The determination of hydroscopicity. Intern. Mitt. Bodenkunde. 1: 463.
42. Murry, H. D. 1921. The coagulation of colloids by electrolytes; Chemical News. 123: 277.
43. Neidle, M., Barab, J. 1917. Studies in dialysis. J. Am. Chem. Soc. 39: 80.
44. Oden, S. 1919. The coagulation of clay and the protective action of humus acids. J. Landw. 67: 197-208.
45. Ormondy, W. R. 1920. Electrical properties of clay suspensions. J. Soc. Chem. Indus. 39: 230, 38 T.
46. Patrick, W. H. McGavock, J. 1920. Adsorption of sulfur dioxide by silica gels. J. Am. Chem. Soc. 42: 946.
47. Powis, F. 1915, Negative colloidal ferric hydroxide. Jour. Chem. Soc. Trans. 107: 818.

48. Ruer, R. 1905. Uber die Bindung des Chlors in kolloidalen Losungen der Metallhydroxyde. Anorg. Chem. **43**: 85.
49. Reis, H. 1908 Clays. p. 125-9.
50. Rholand, P. 1914. Die Kolloide der tonigen und Hummusboden. Zeit. Forst. u. Landw. **12**: 380-5.
51. Robbins, W. J., 1922. Private communication.
52. Schloessing, Th. 1874. Sur la constitutions des argile. Compt. Rendu. **79**: 376-80.
53. Schloessing, Th. 1901. Reserches sur l'etat de alumine dans des terres vegetables. Compt. Rendu. **132**: 1203.
54. Smith, Otto. M. 1920. The coagulation of clay suspensions and silicic acid. J. Am. Chem. Soc. **42**: 400-72.
55. Splichal, J. 1921. The colloidal system silica-alumina. Chem. List. **15**: 53-6, 88-90, 110-3, 140-3, 164-7.
56. Stevenson, R. E. 1921. Effect of organic matter on soil reaction. Soil Science **12**: 145.
57. Svedberg, Th., Anderson, H. 1919. Zur Messmethodik der elektrischen Kataphorese. Koll. Zeit. **24**: 156.
58. Swanson, C. L., Latshaw, W. L., Tague, E. L. 1921. The relation of the calcium content of soils to their reaction. J. Ag. Res. **20**: 855.
59. Tacke, B., Immendorff, H. 1898. Untersuchungen uber die Phosphorbindung des Moorbodens. Landw. Jahrb. Supplement. **27**: 303.
60. Taylor, W. W. 1916. The Chemistry of Colloids. Edward Arnold Co. London p. 80.
61. Tempany, H. A. 1917. The shrinkage of soils. J. Ag. Sci. **8**: 312-20.
62. Thomas, A. F., Foster, S. B. 1922. The colloid content of vegetable tannin extracts. J. Ind. Eng. Chem. **14**: 191.
63. Ulpiani, C. 1913. Lateritization of the soil under arid conditions. Staz. sper. agr. ital. **45**: 629. Chem. Abs. 1913 p. 2820.
64. Vageler, P. 1913 Die Entstehung Des Laterites. Mitt. D. Land. Gess. Heft 26 S. 385.
65. Weiser, H. B. 1919. Adsorption by precipitates. J. Phy. Chem. **23**: 205, **24**: 30.
66. Weiser, H. B. 1920. Hydrous oxides. J. Phy. Chem. **24**: 277, 505.
67. Weiser, H. B. 1921. Adsorption by precipitates. J. Phy. Chem. **25**: 399.
68. Wolkoff, M. I. 1916. Flocculation of soil colloids. Soil Science **1**: 585.
69. Wolkoff, M. I. 1920. Effects of various salts and lime upon evaporation, capillary rise and distribution of water in some agricultural soils. Soil Sci. **9**: 409.

AUTOBIOGRAPHY

I, Richard Bradfield, was born on a farm near West Jefferson in Madison County, Ohio, April 29, 1896. I received my elementary education in the public and high schools of the same county, and my undergraduate education at Otterbein College from which I obtained the Degree of Bachelor of Arts in 1917. I spent the years 1918-19 and 1919-20 at full time, resident graduate work at Ohio State University and the years 1920-21, 1921-22 at full time research at the University of Missouri. I received the Degree of Doctor of Philosophy from the Ohio State University in 1922. My thesis work was done *in absentia* at the University of Missouri.